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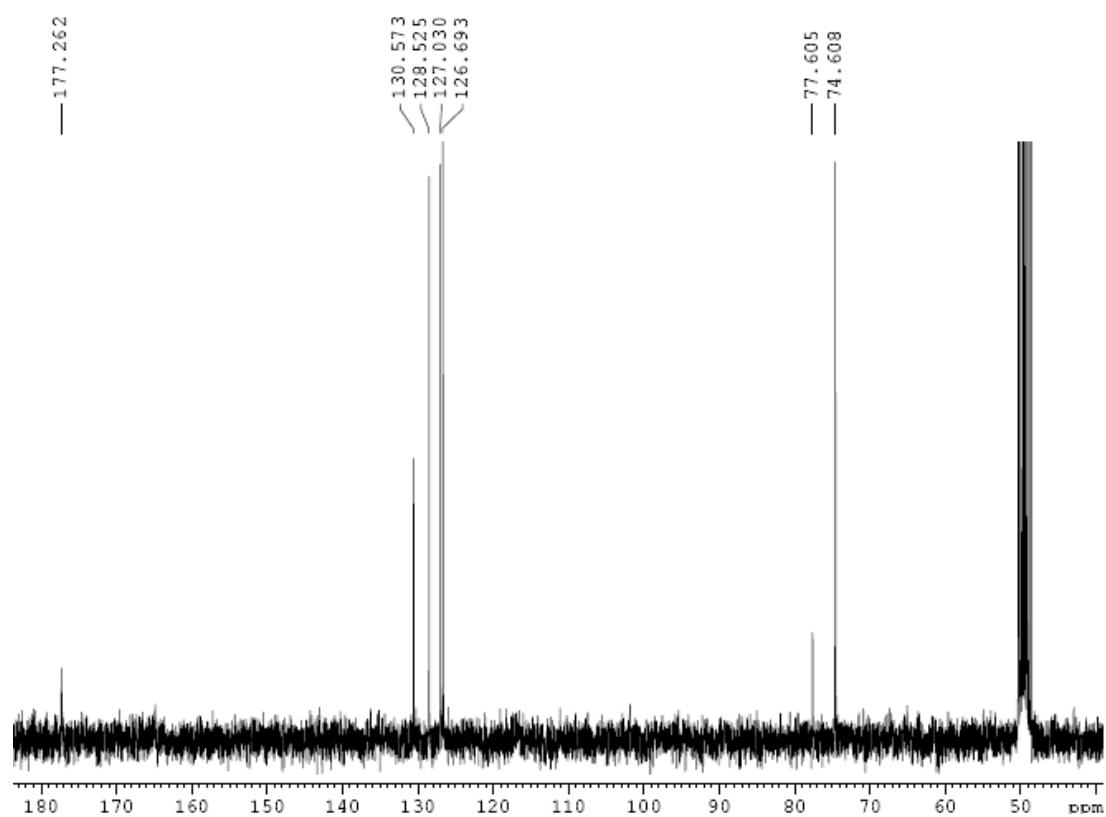
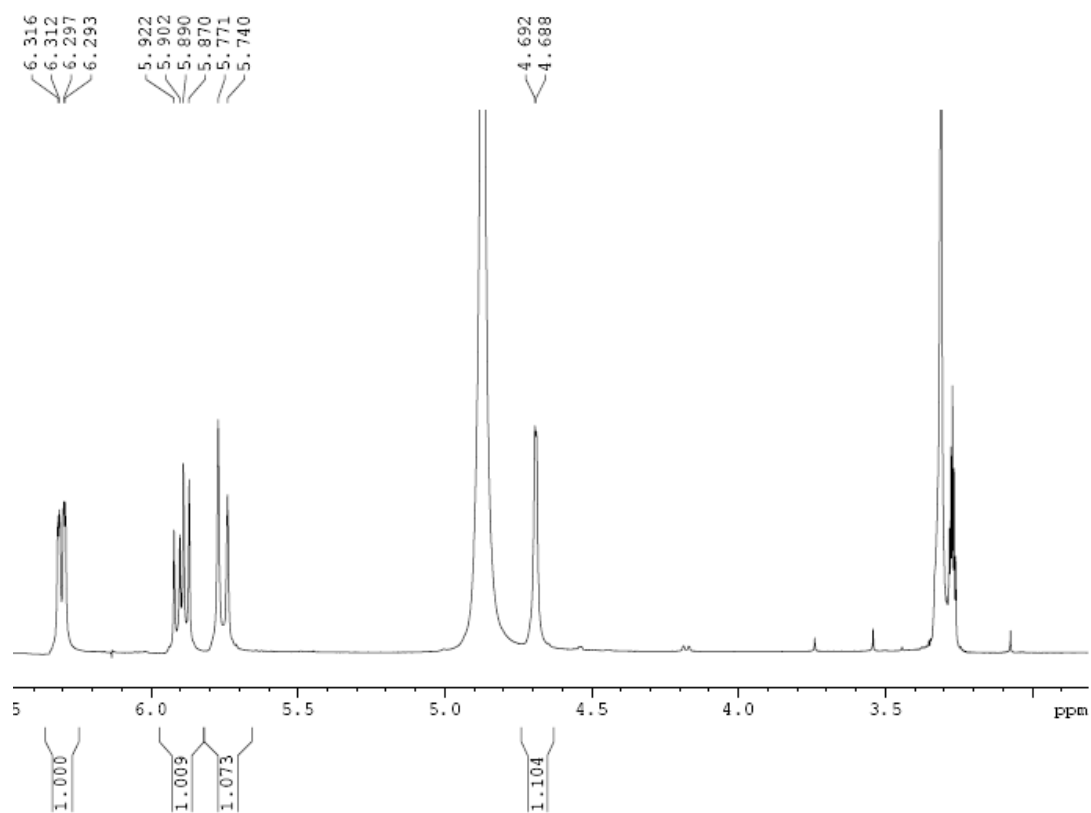
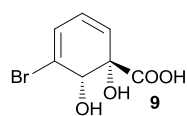
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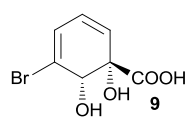
# Electronic Supporting Information

Expanding the chiral pool: oxidation of 3-bromobenzoic acid by *R. eutrophus* B9 allows access to new reaction manifolds.

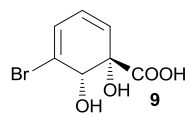
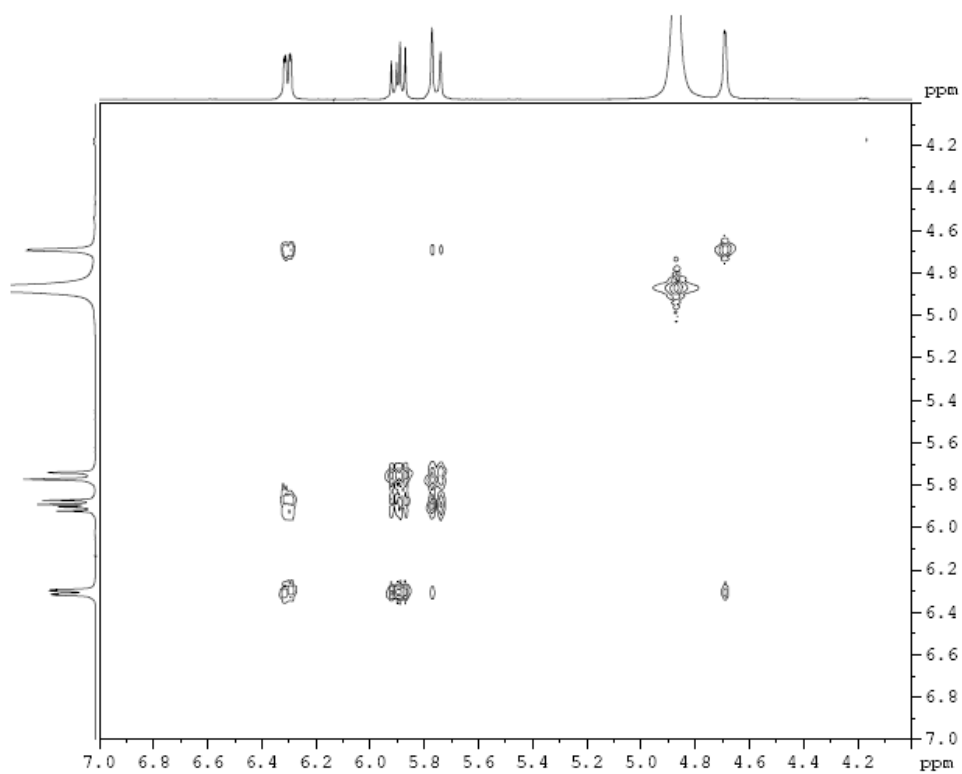
Julia A. Griffen, Amélie M. Le Coz, Gabriele Kociok-Köhn, Monika Ali Khan, Alan J. W. Stewart and Simon E. Lewis\*

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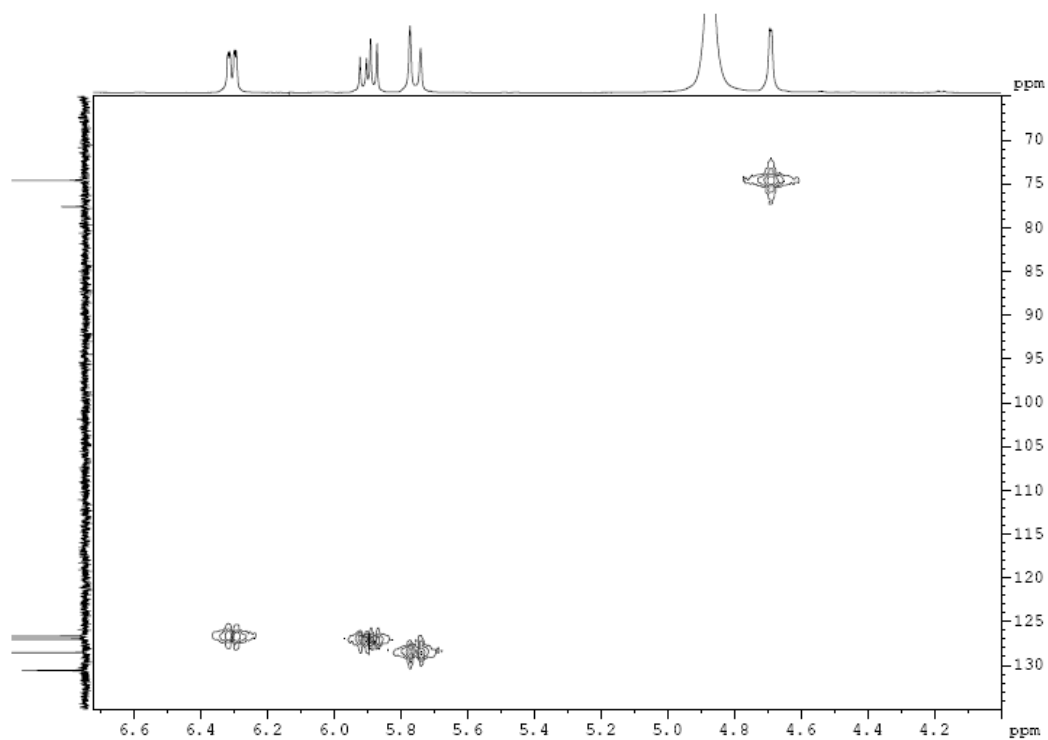


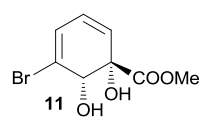


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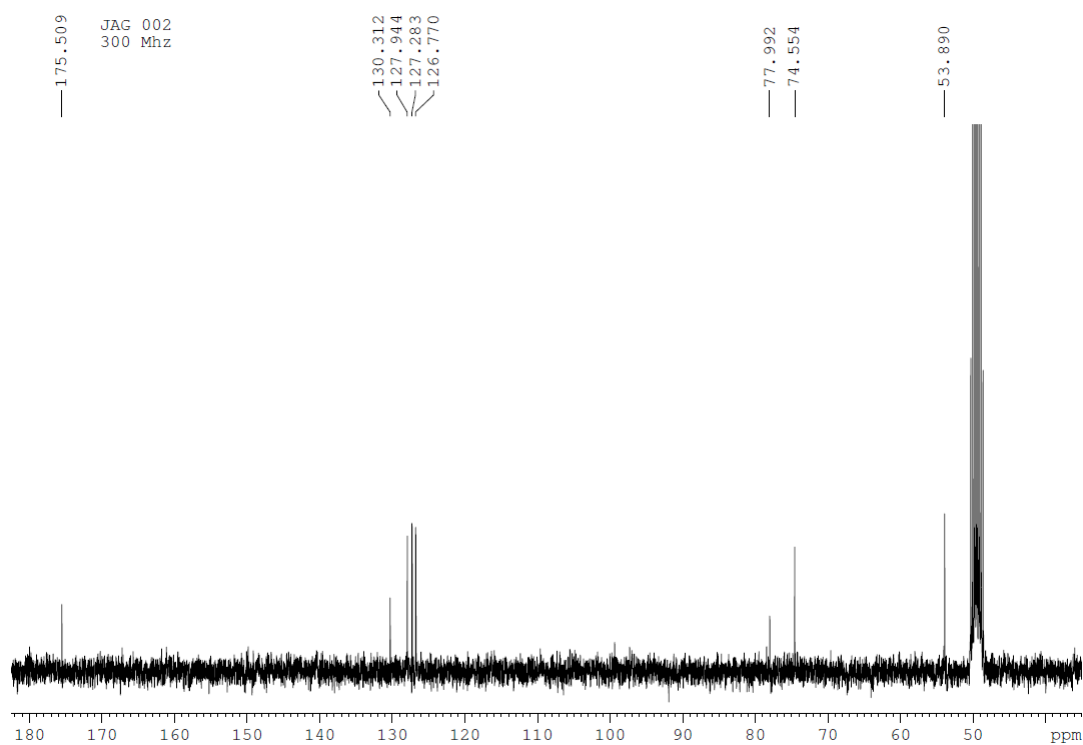
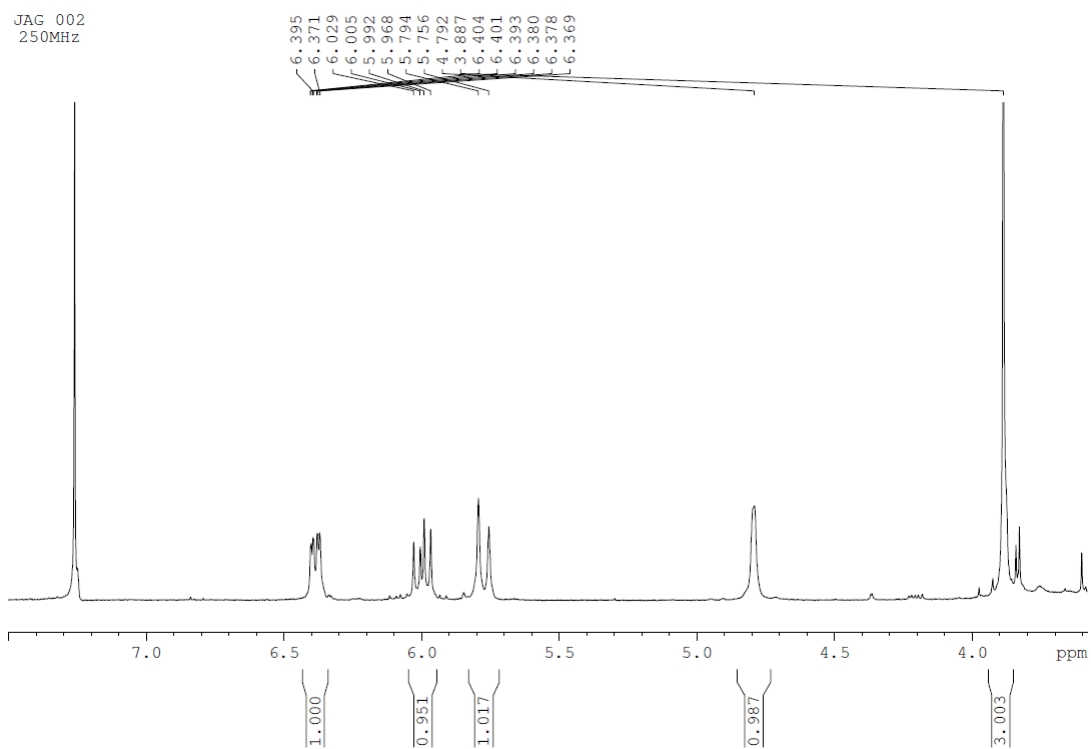


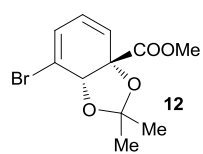
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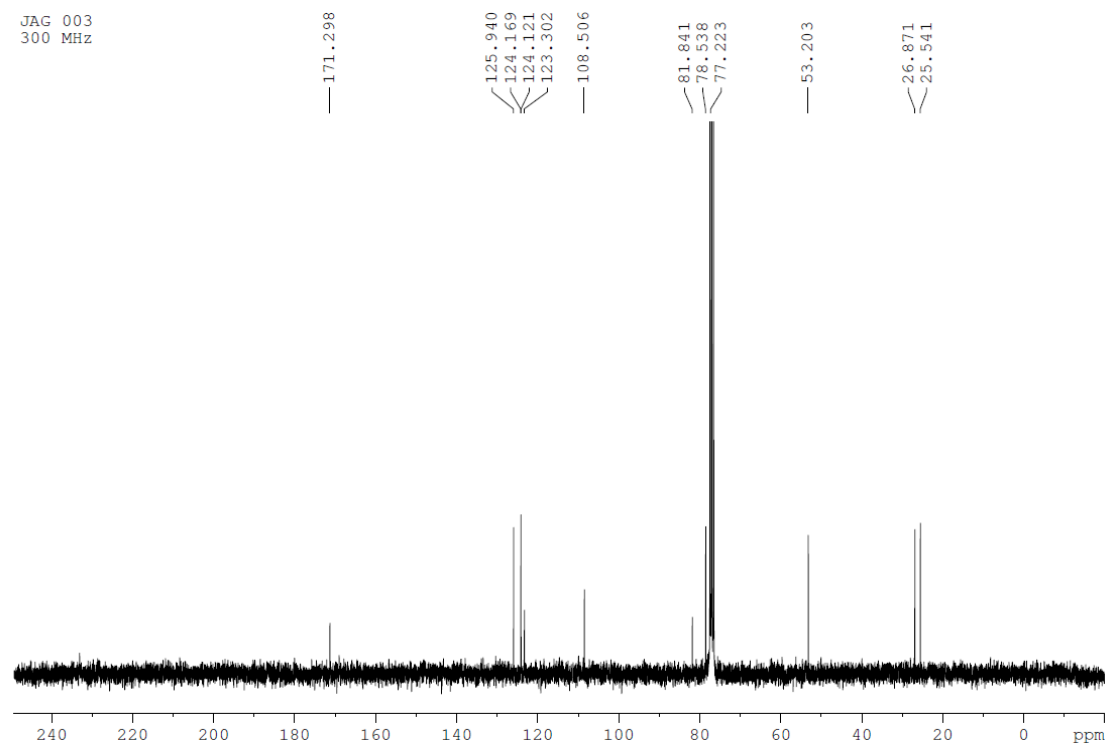
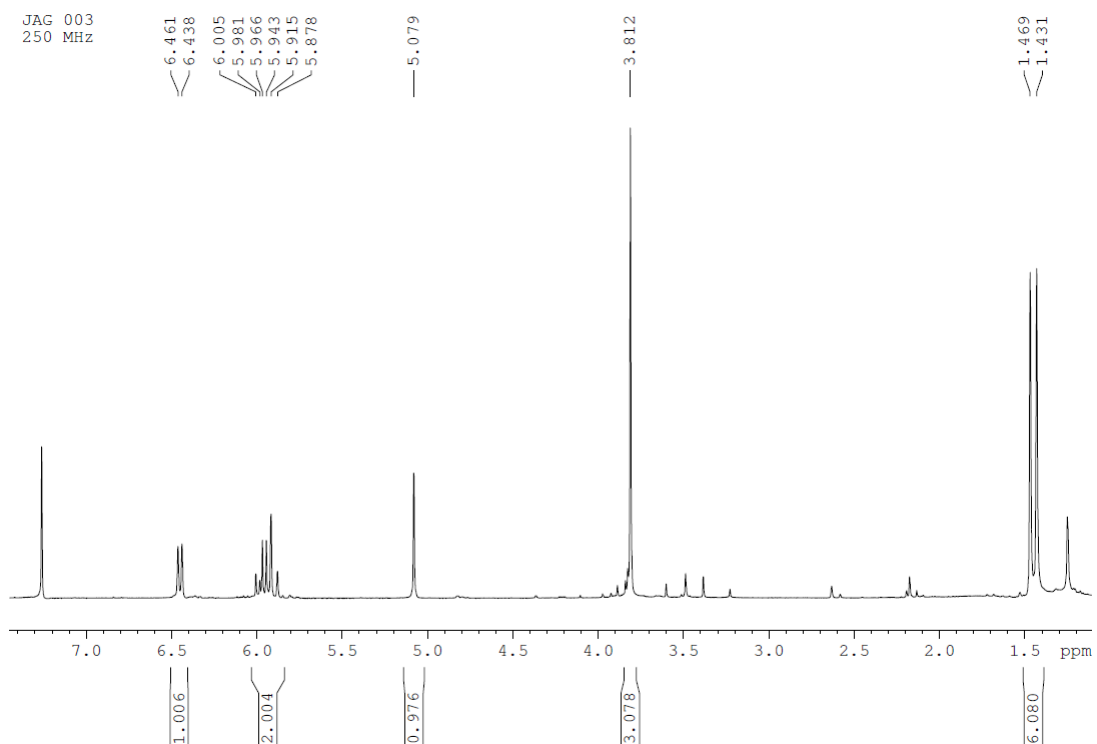


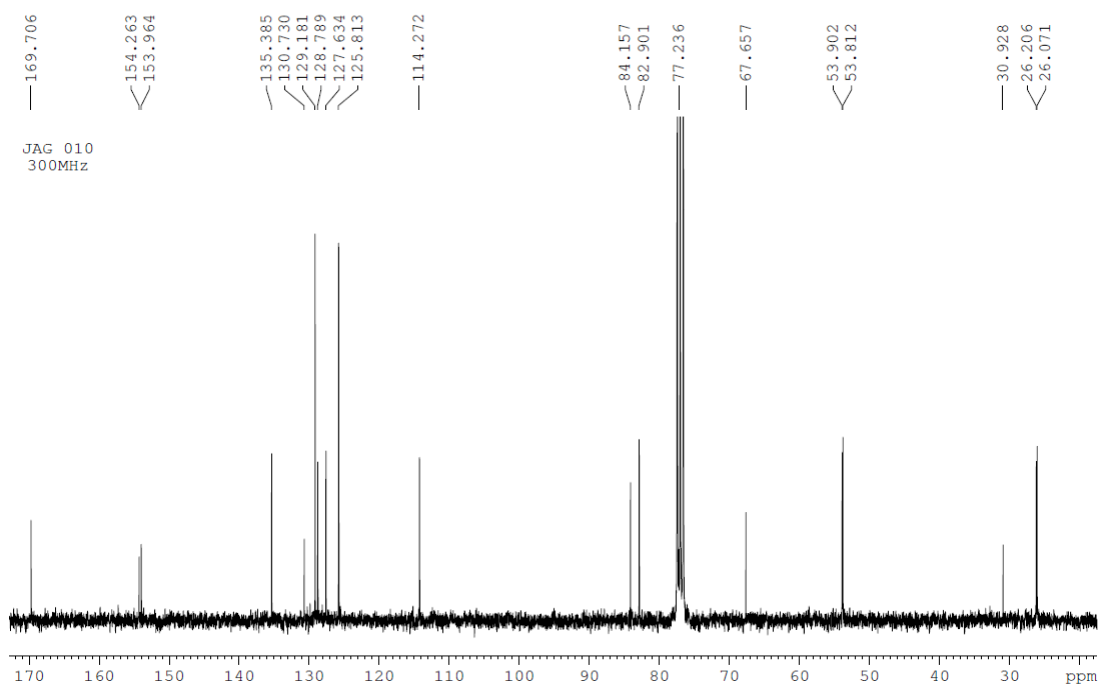
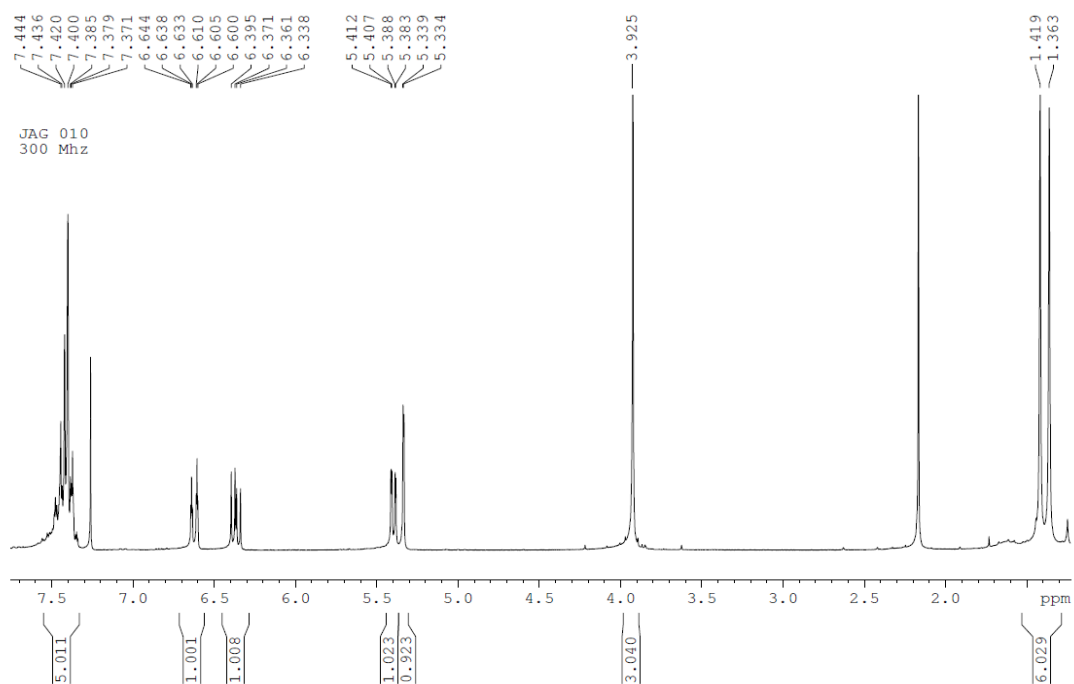
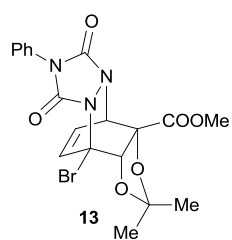
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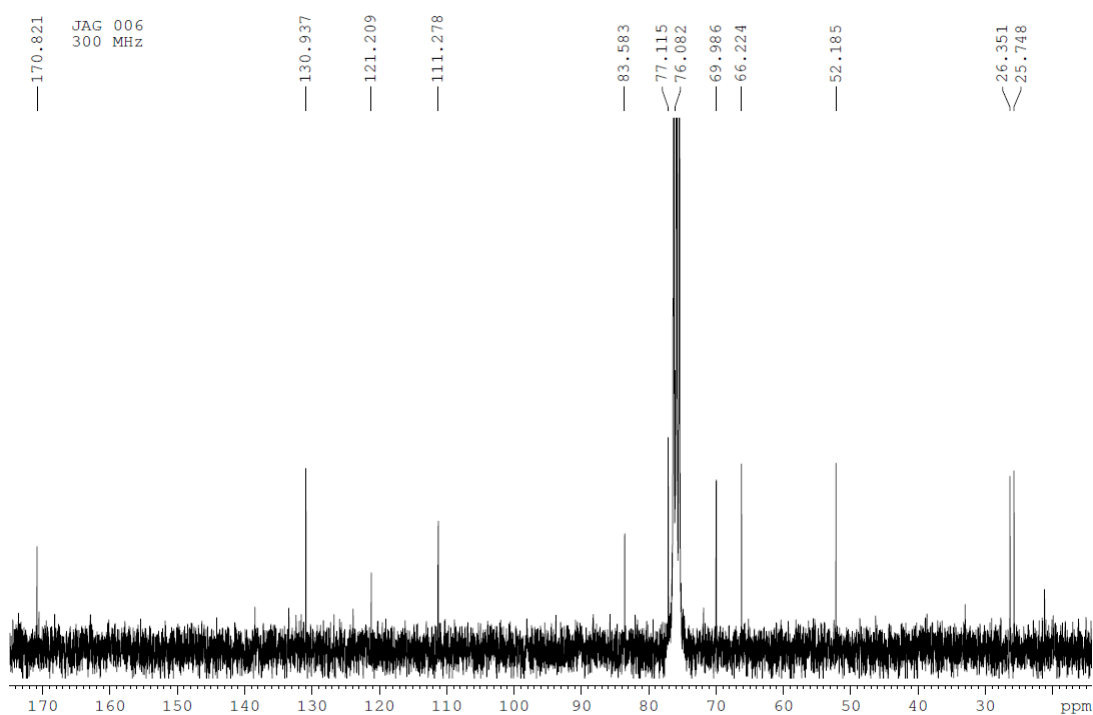
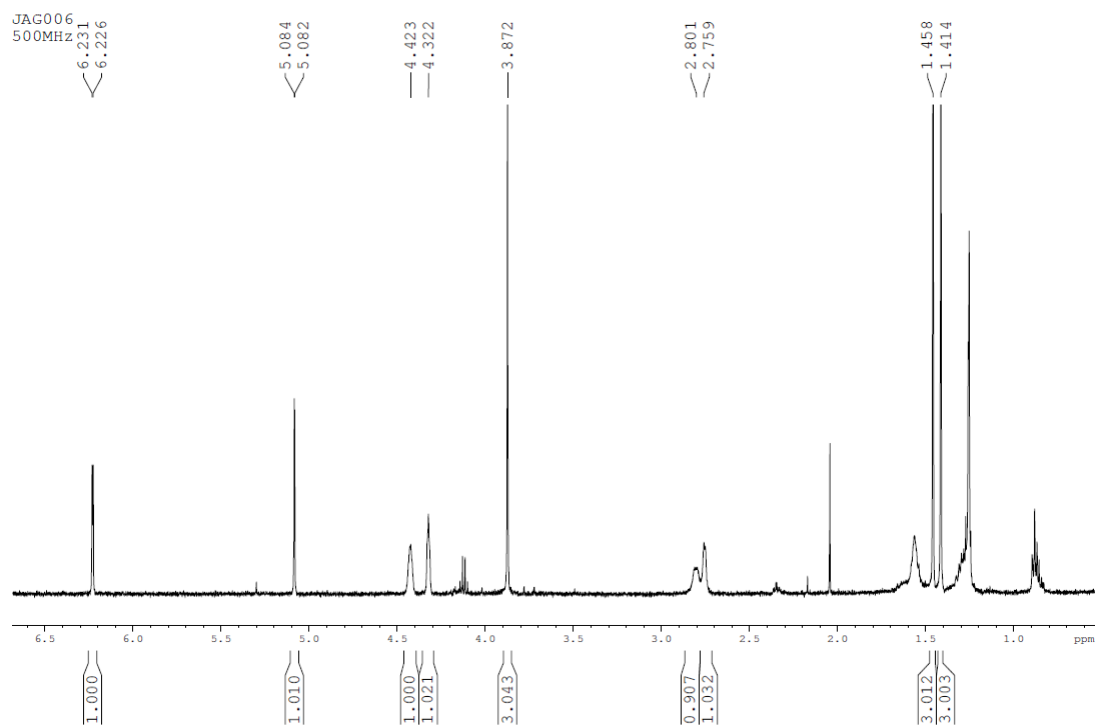
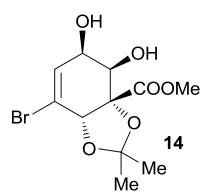




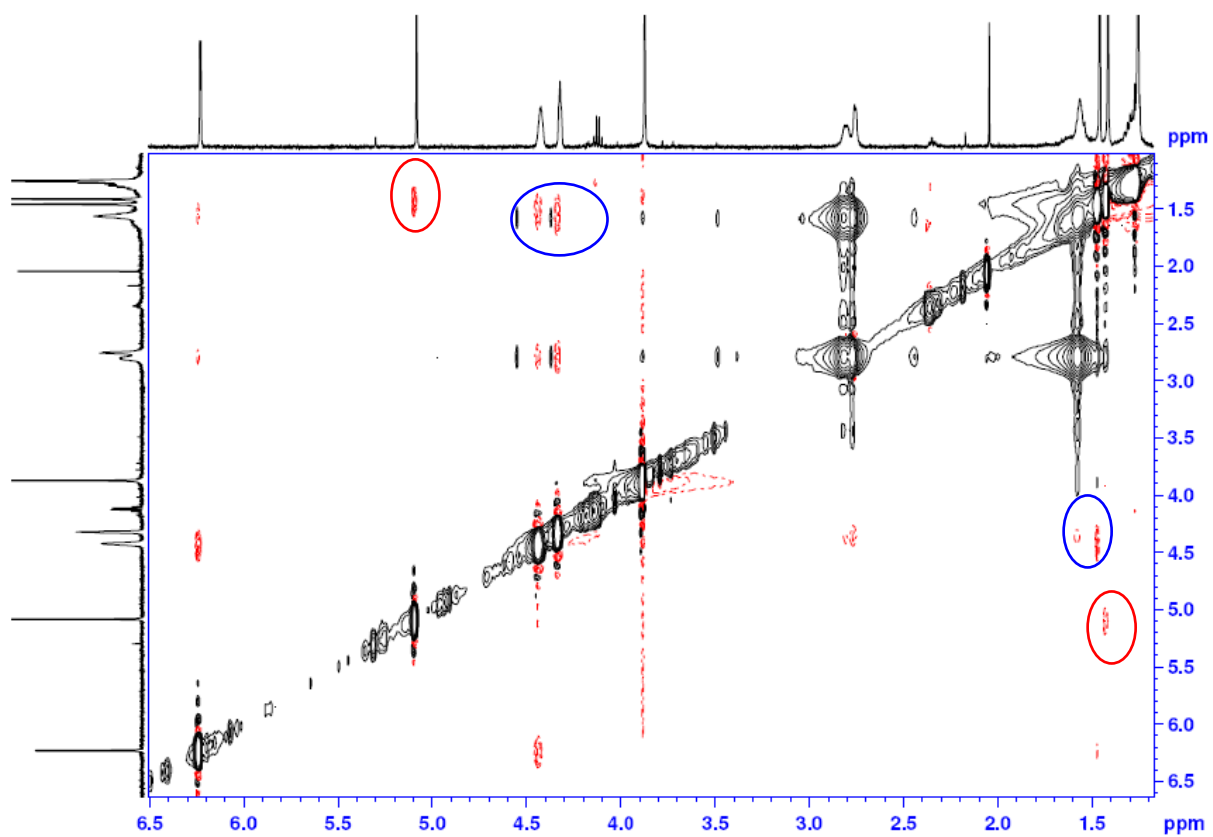
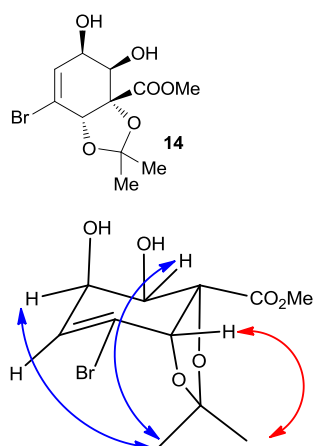
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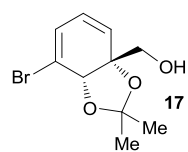




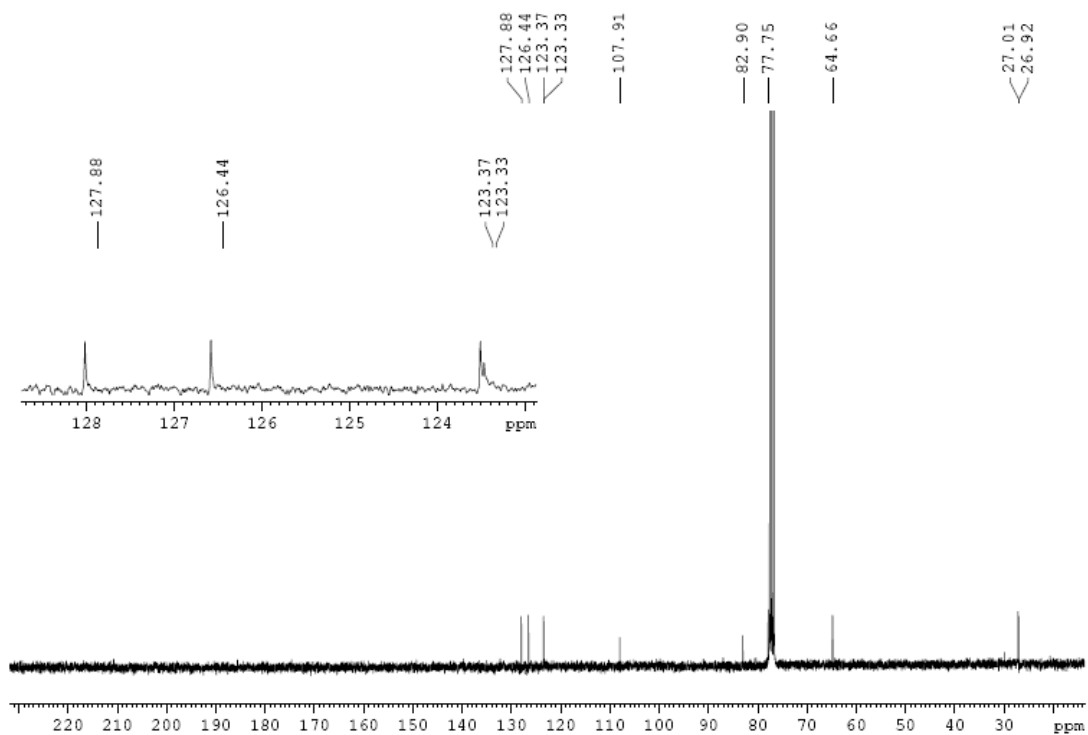
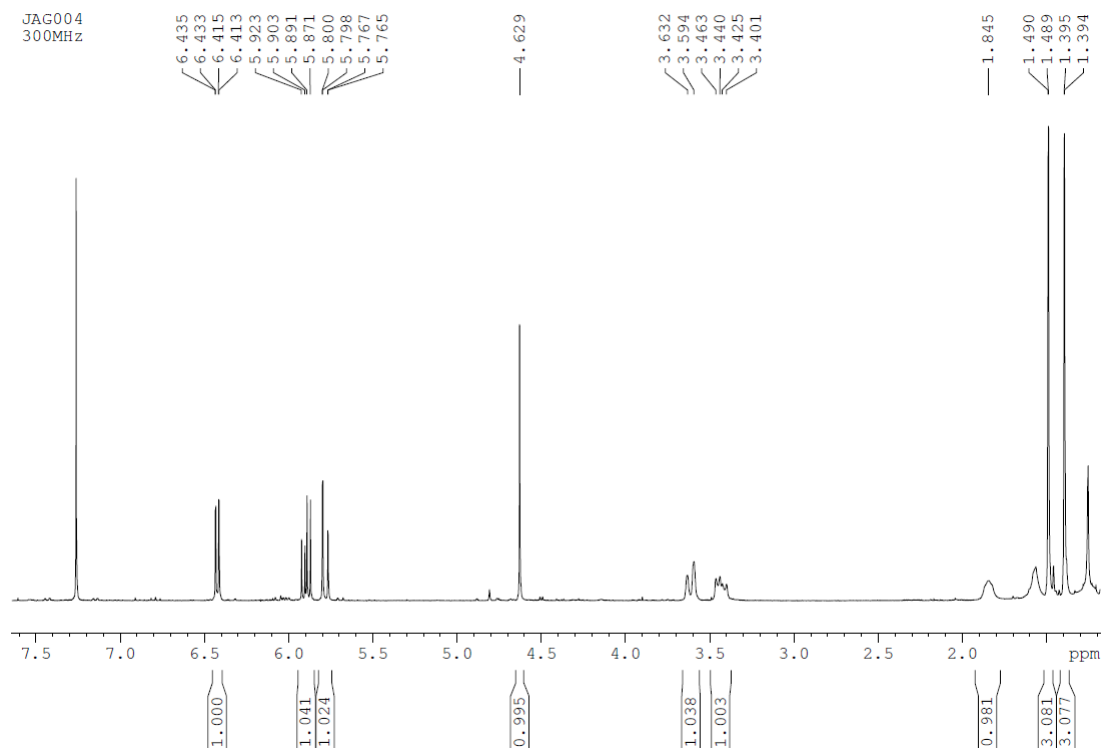


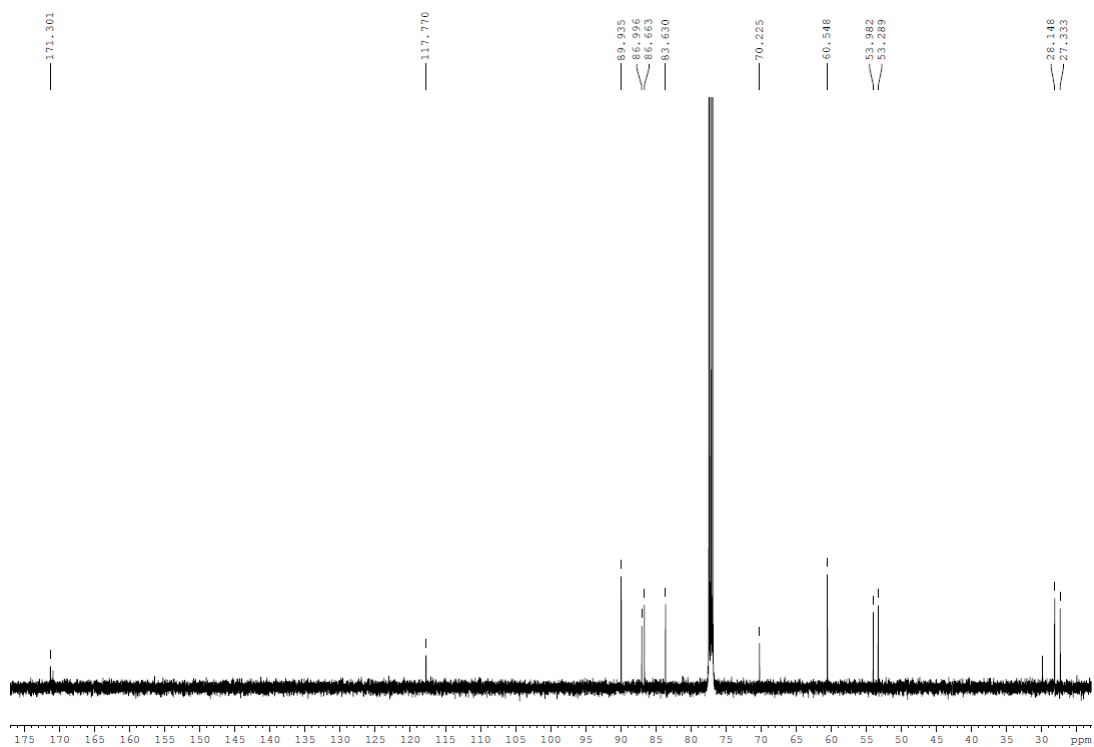
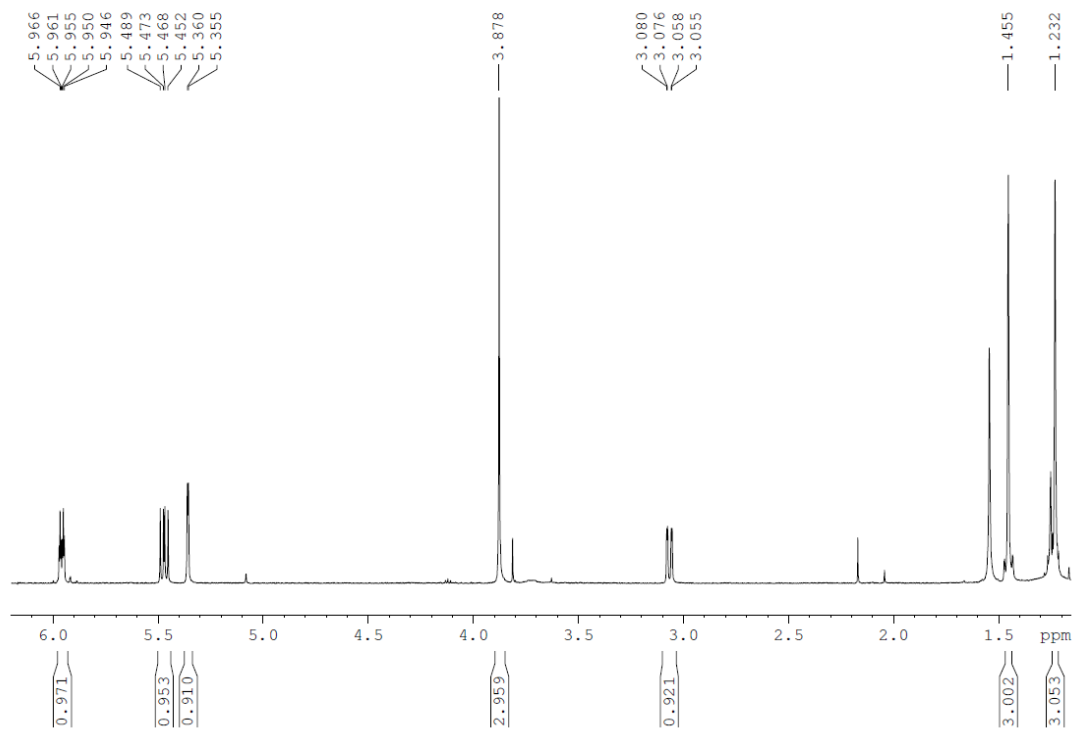
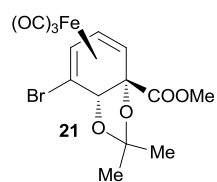


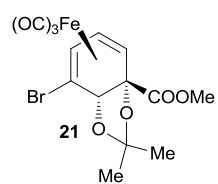




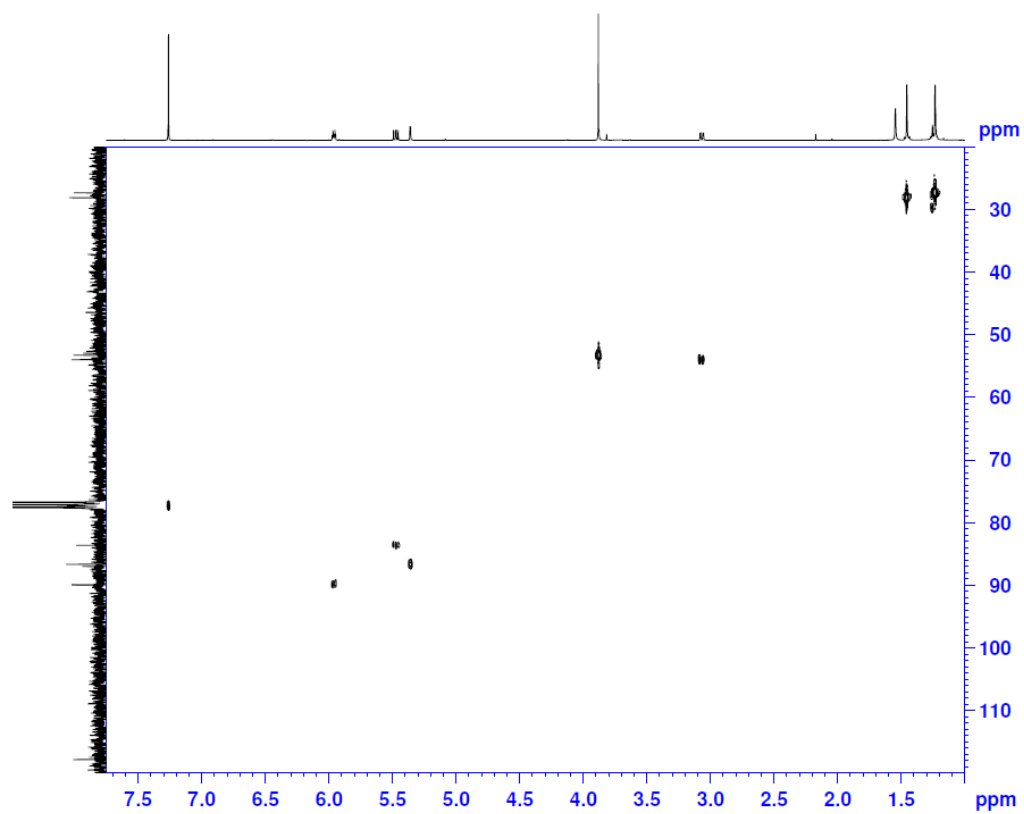
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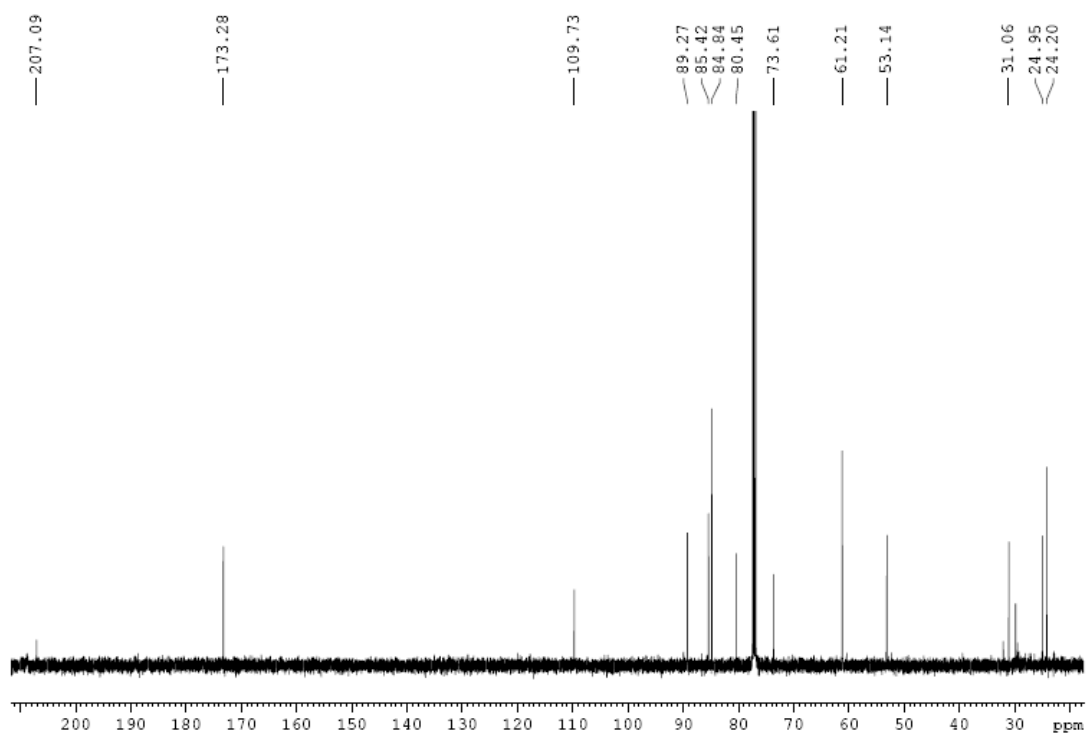
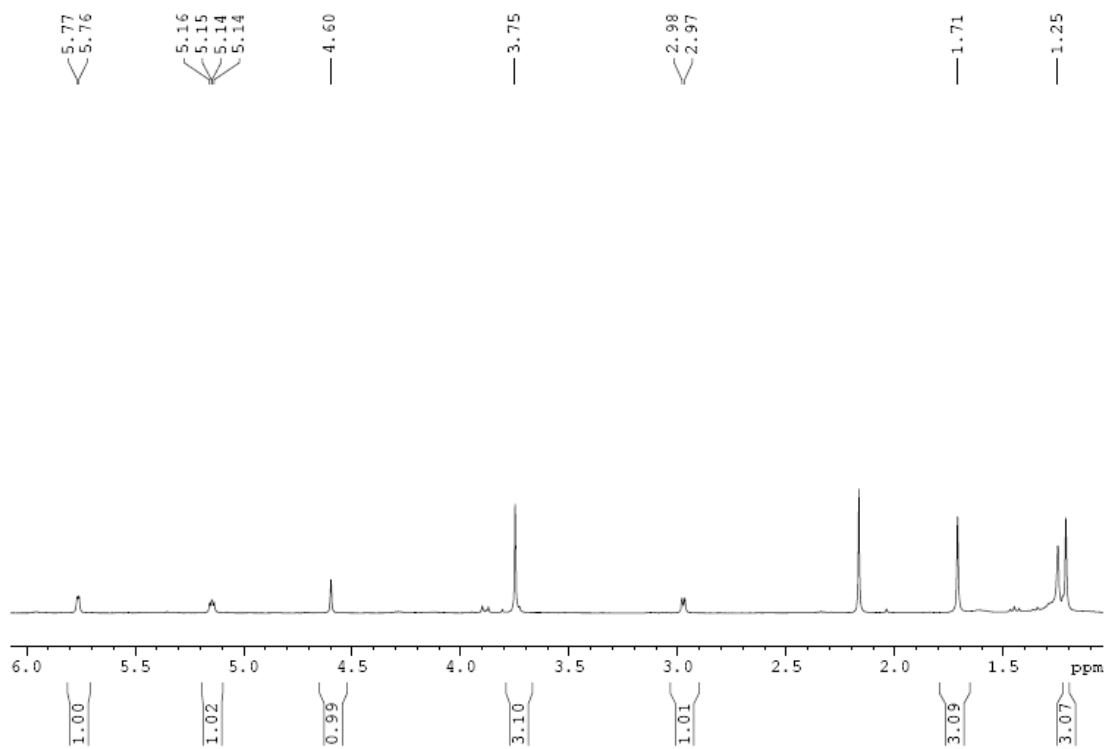
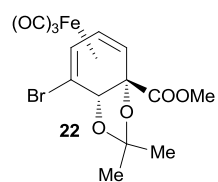


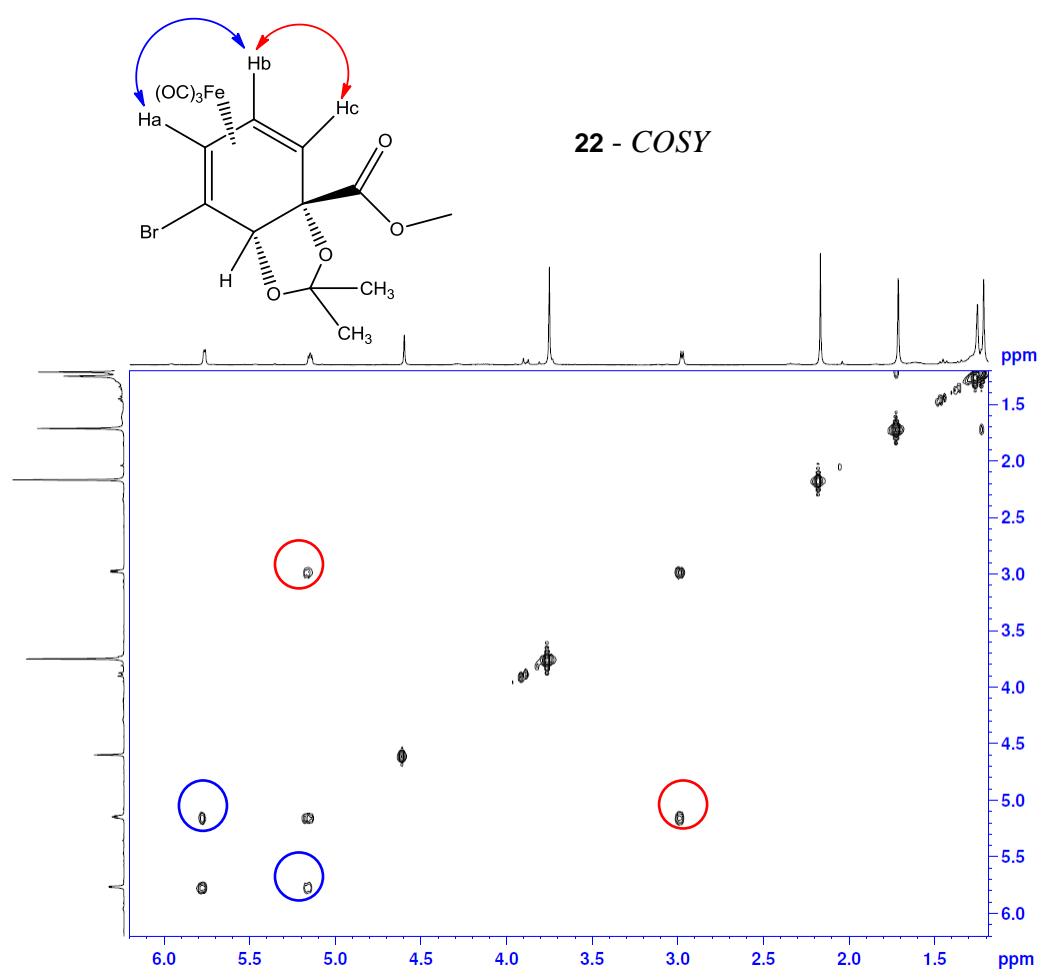




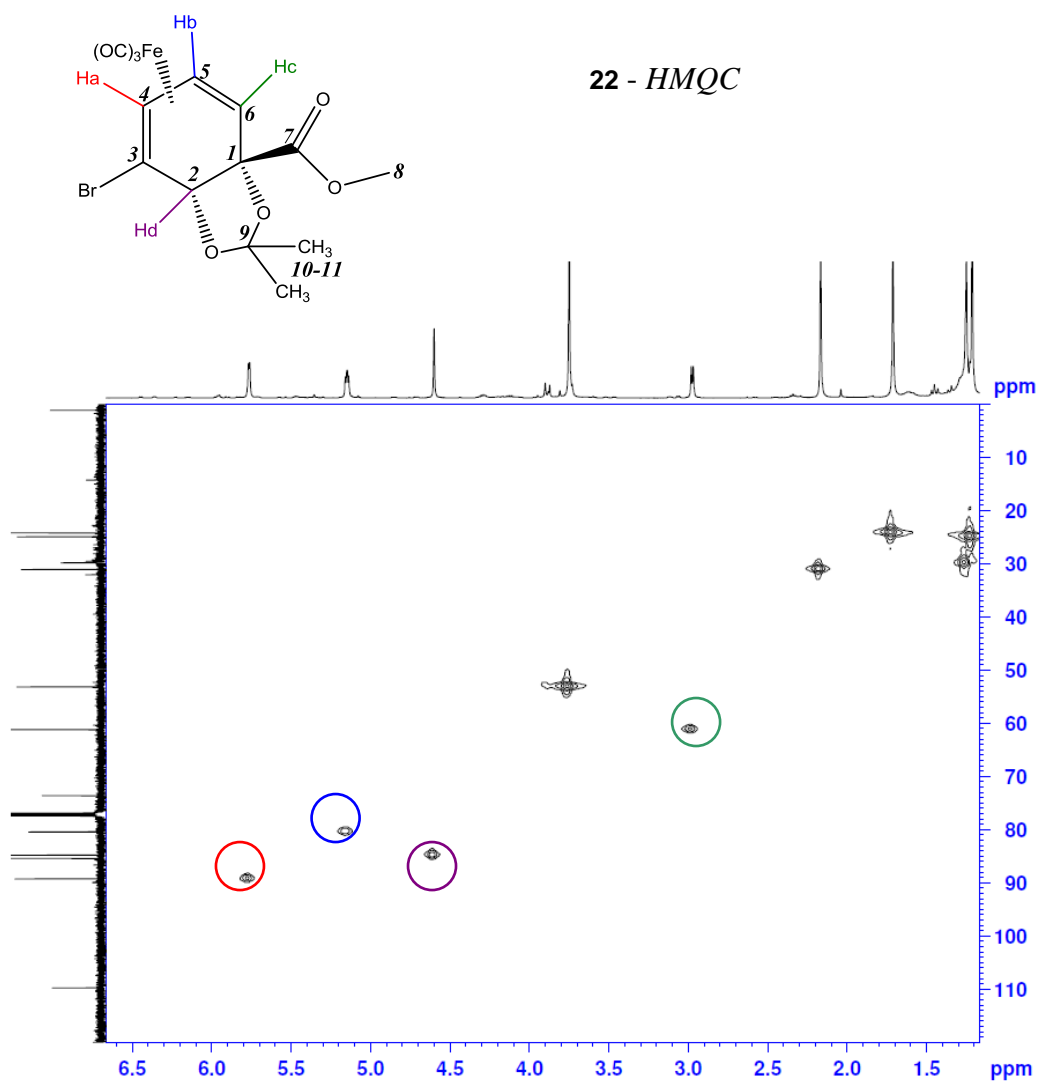
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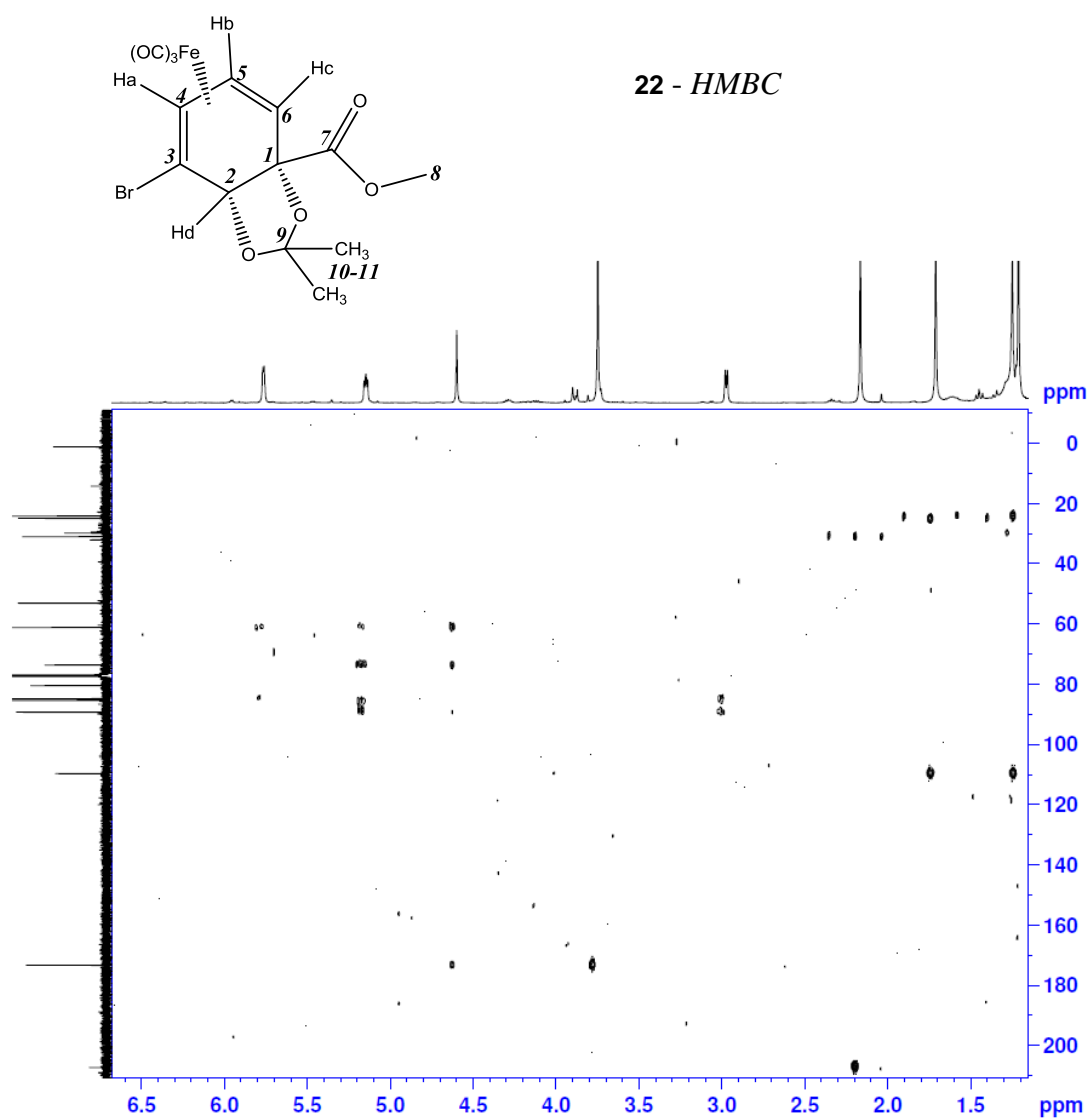




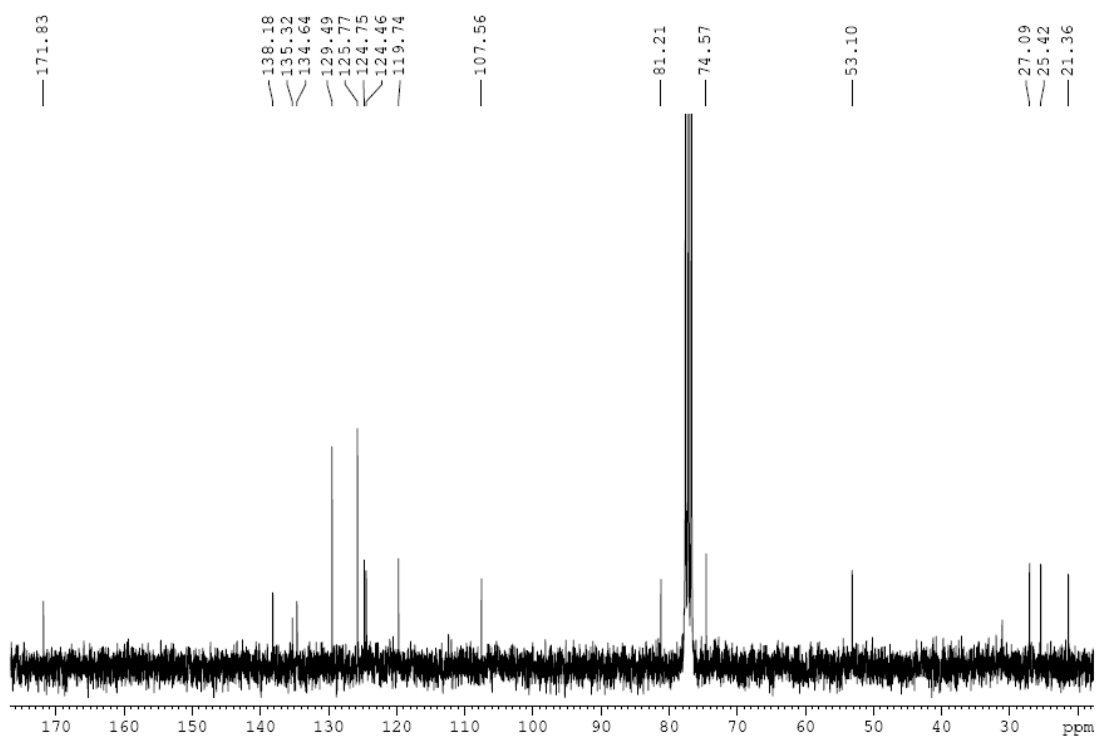
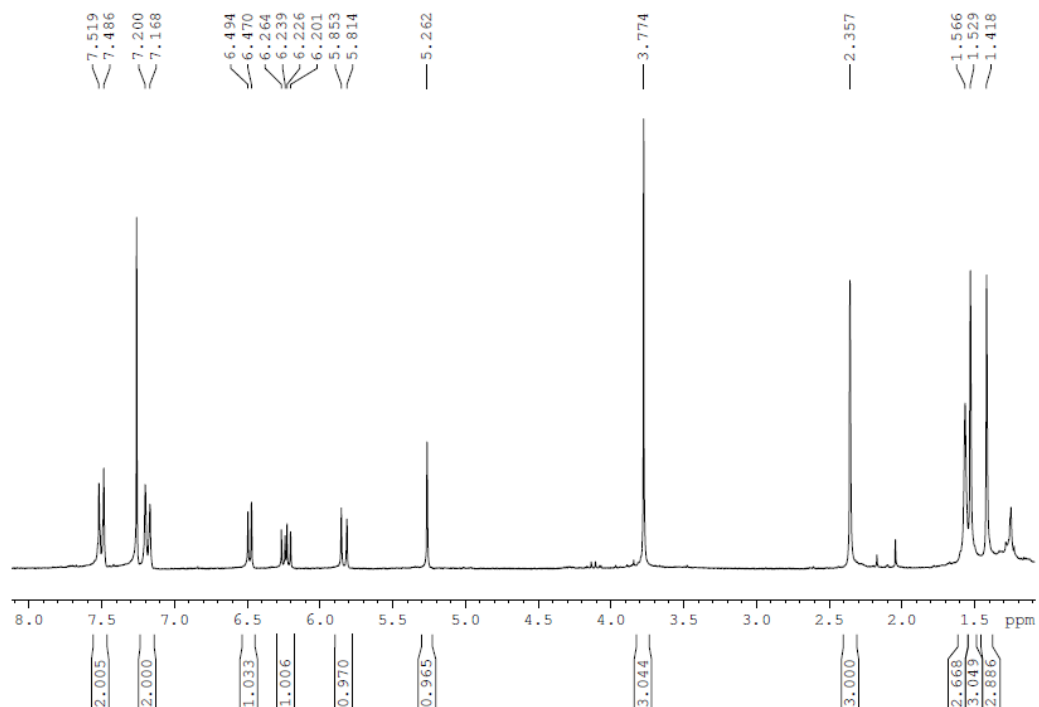
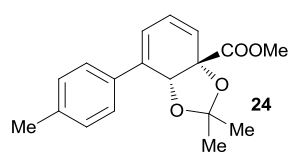


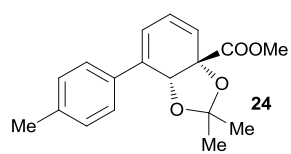
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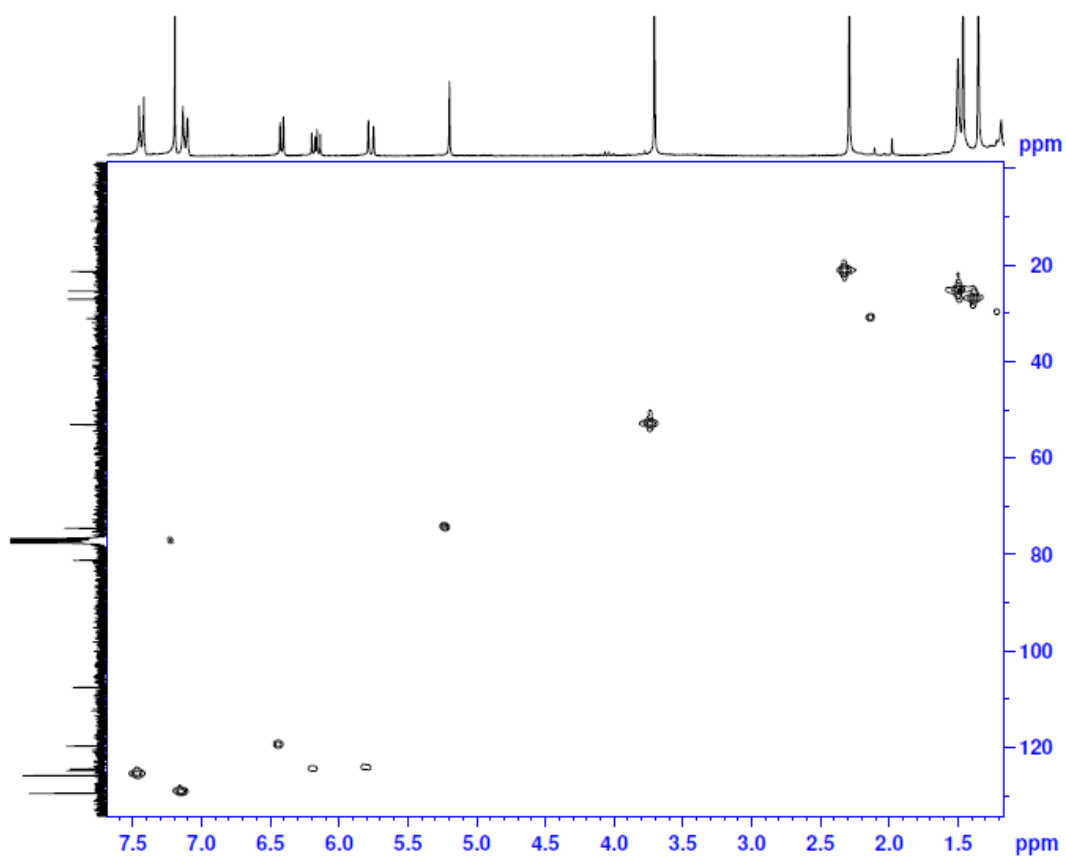


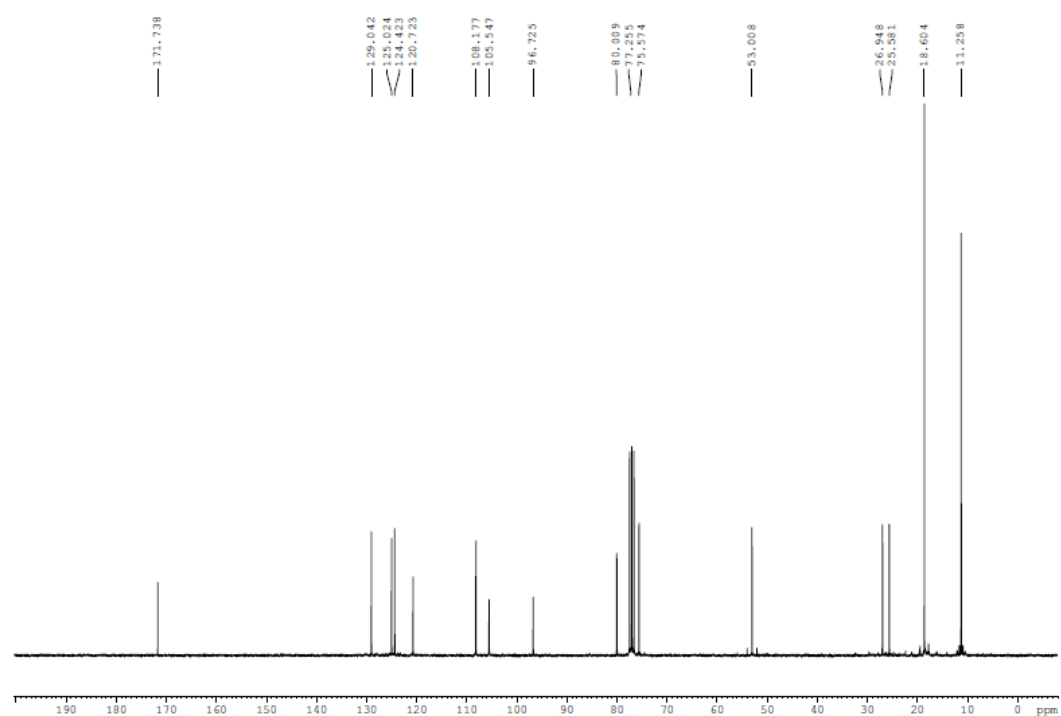
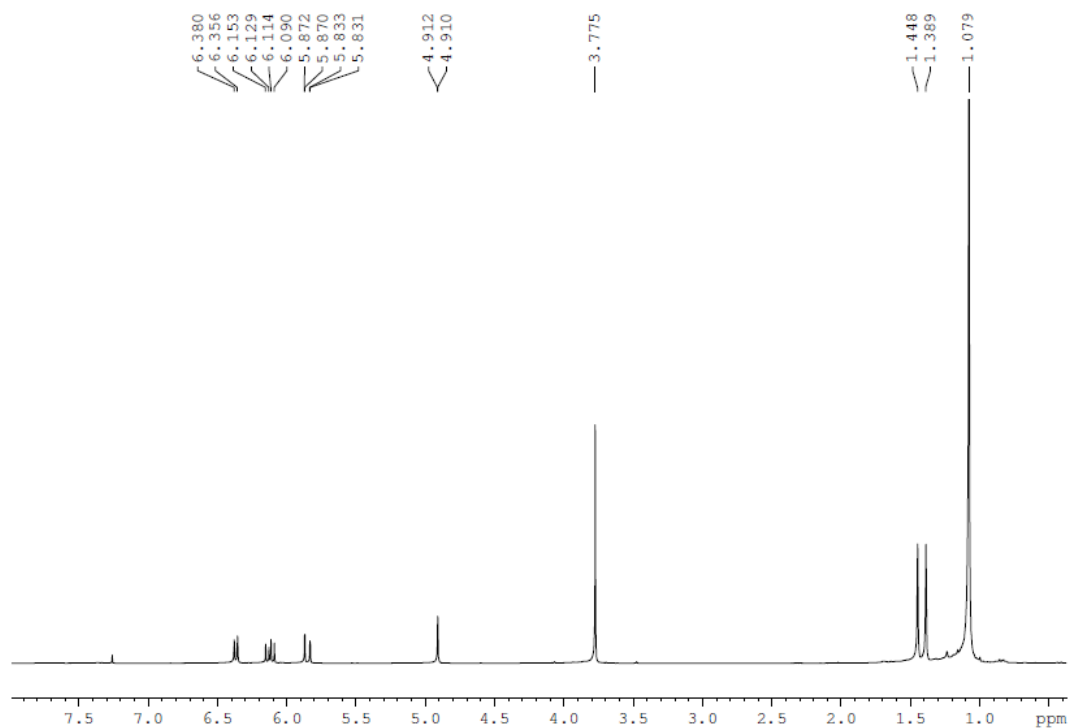
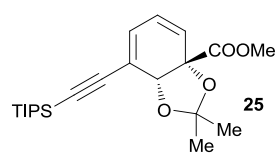


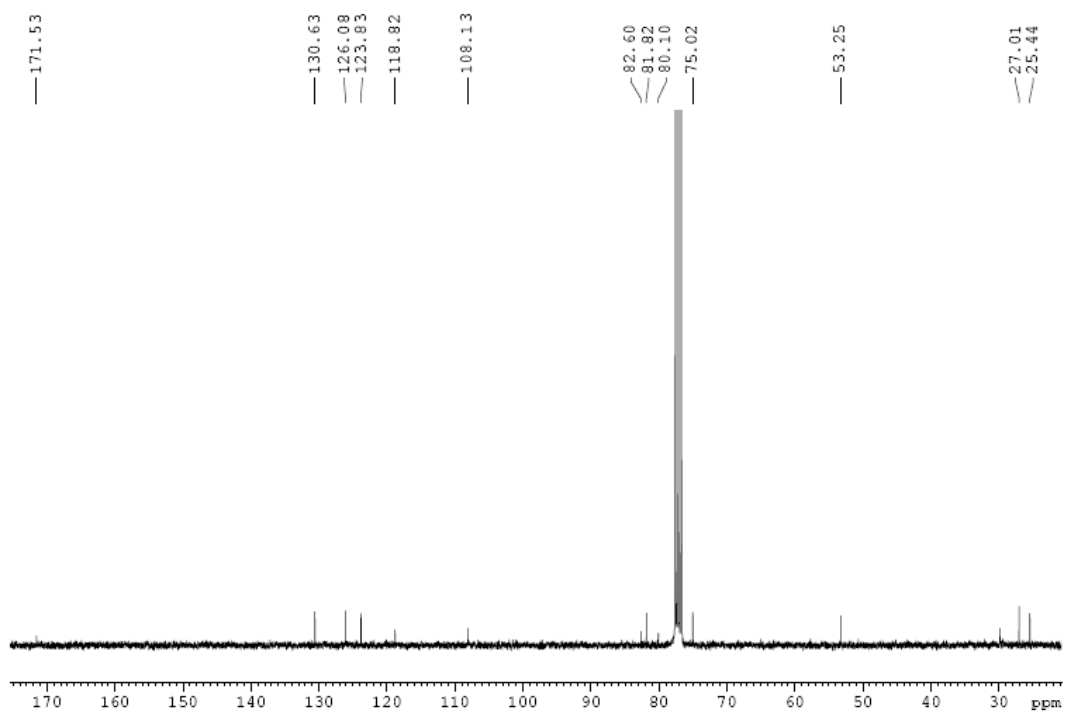
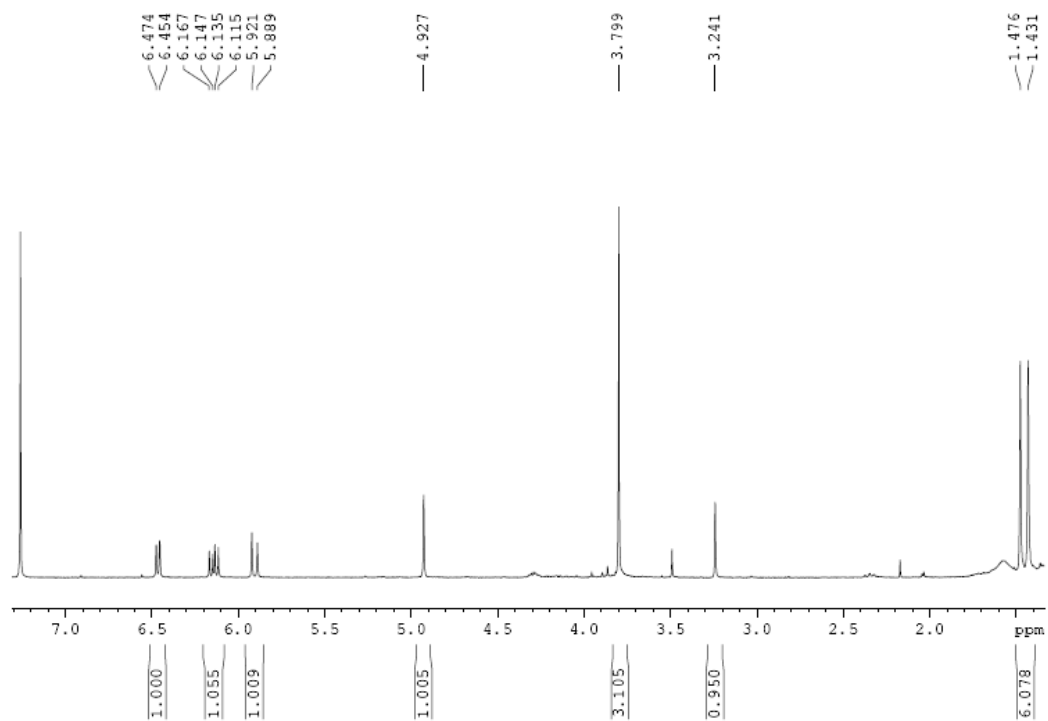
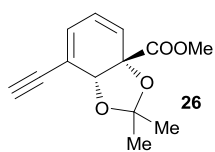


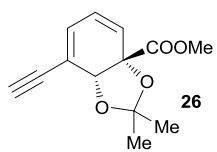


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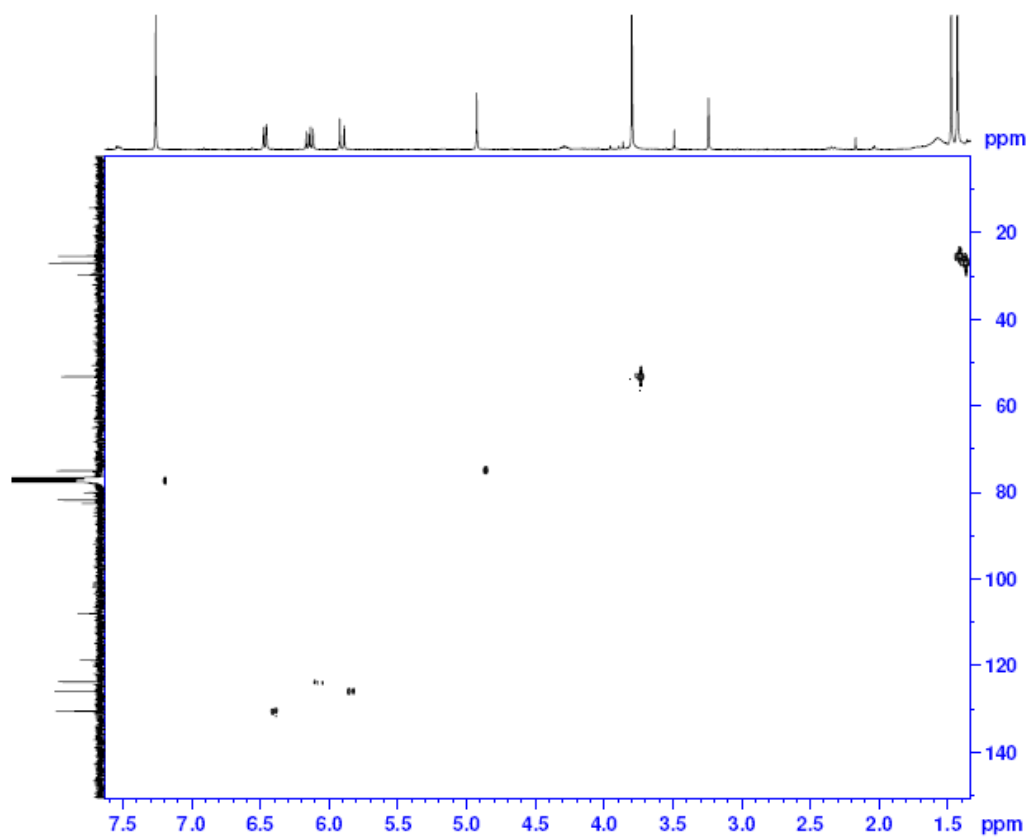


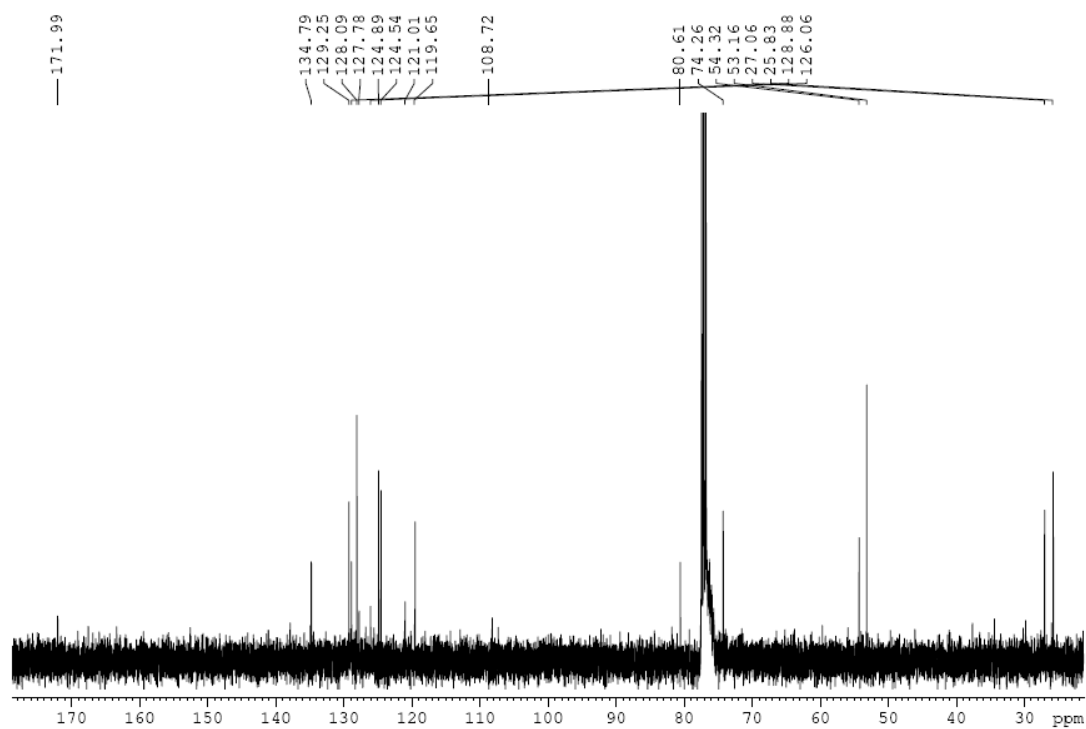
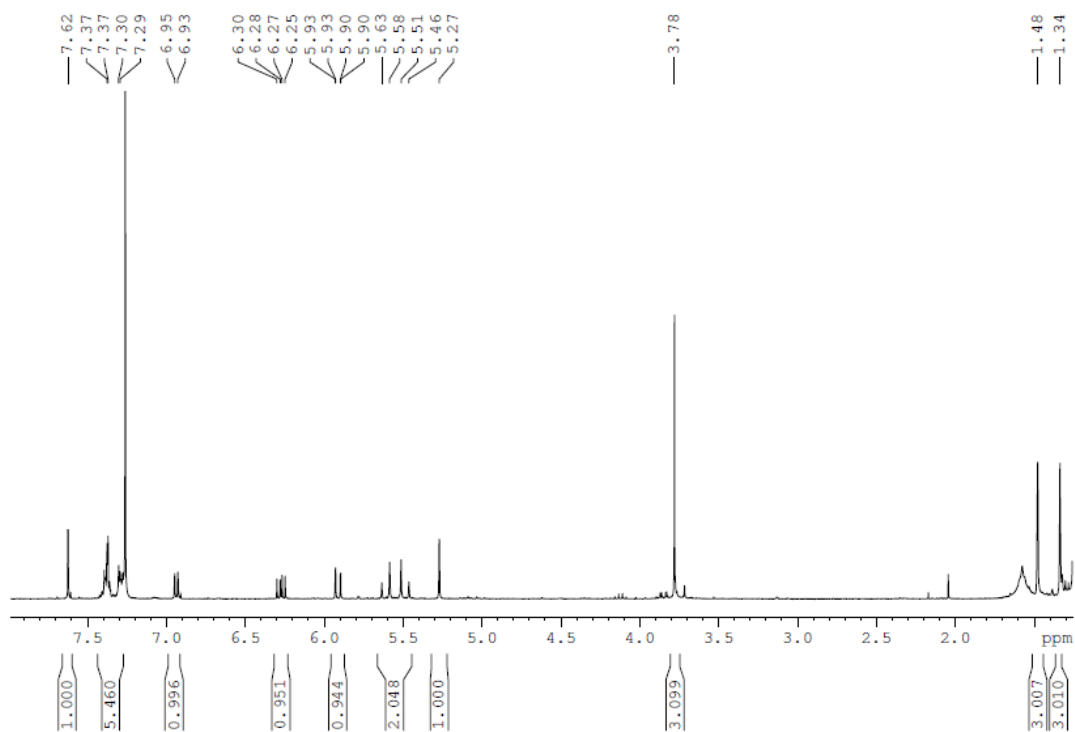
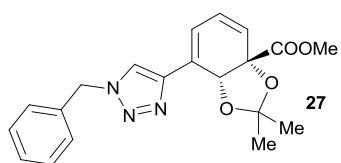


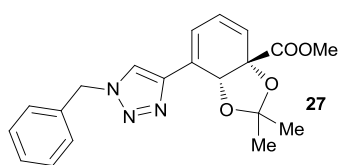




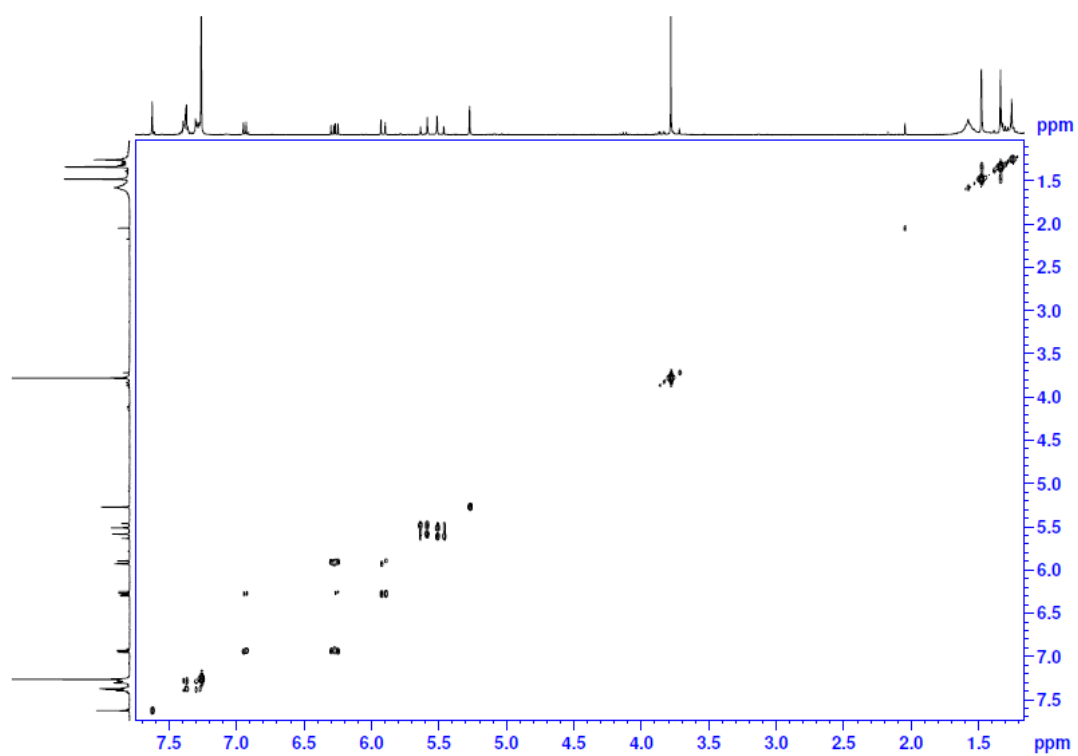
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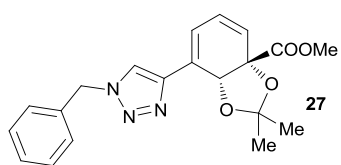






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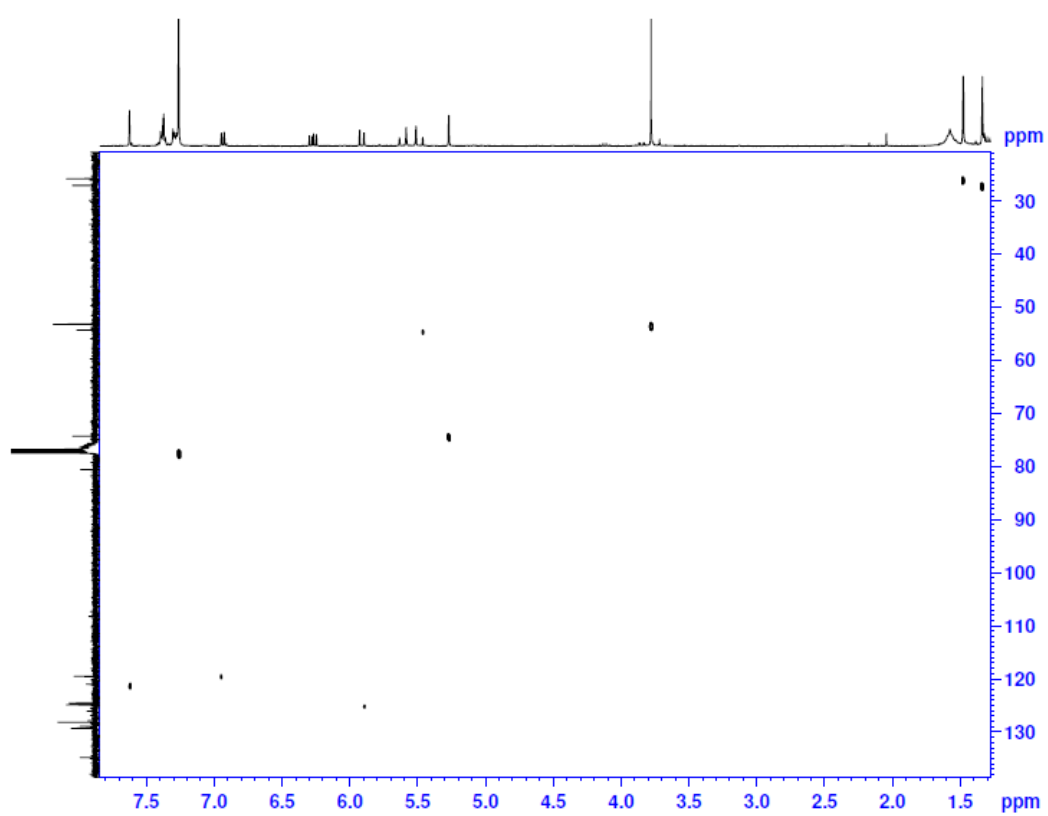




Table S1. Crystal data and structure refinement for **13**.

Identification code	p10sell
Empirical formula	C19 H18 Br N3 O6
Formula weight	464.27
Temperature	150(2) K
Wavelength	1.54184 Å
Crystal system, space group	Hexagonal, P 6 <sub>5</sub>
Unit cell dimensions	a = 27.8075(4) Å    alpha = 90 deg. b = 27.8075(4) Å    beta = 90 deg. c = 6.47080(10) Å    gamma = 120 deg.
Volume	4333.24(11) Å <sup>3</sup>
Z, Calculated density	6, 1.067 Mg/m <sup>3</sup>
Absorption coefficient	2.196 mm <sup>-1</sup>
F(000)	1416
Crystal size	0.40 x 0.20 x 0.10 mm
Theta range for data collection	4.86 to 66.74 deg.
Limiting indices	-29<=h<=33, -33<=k<=33, -7<=l<=6
Reflections collected / unique	52878 / 4920 [R(int) = 0.0752]
Completeness to theta = 66.74	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8103 and 0.4737
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4920 / 1 / 265
Goodness-of-fit on F <sup>2</sup>	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0850
R indices (all data)	R1 = 0.0418, wR2 = 0.0864
Absolute structure parameter	-0.003(17)
Largest diff. peak and hole	0.324 and -0.221 e.Å <sup>-3</sup>

Table S2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **13**.  
 $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U(\text{eq})$
Br	2656(1)	3496(1)	1396(1)	43(1)
N(1)	3443(1)	4763(1)	5658(4)	32(1)
N(2)	3363(1)	4342(1)	4164(4)	31(1)
N(3)	3941(1)	4384(1)	6624(4)	32(1)
O(1)	3353(1)	5646(1)	1551(5)	52(1)
O(2)	3505(1)	5901(1)	4867(5)	58(1)
O(3)	2296(1)	4960(1)	4150(4)	39(1)
O(4)	2154(1)	4293(1)	1759(4)	41(1)
O(5)	3900(1)	5036(1)	8774(4)	48(1)
O(6)	3680(1)	3703(1)	4114(4)	39(1)
C(1)	3764(2)	6209(2)	931(9)	78(2)
C(2)	3265(1)	5555(1)	3586(6)	41(1)
C(3)	2808(1)	4963(1)	4040(5)	34(1)
C(4)	1944(1)	4643(1)	2445(6)	39(1)
C(5)	1985(2)	5028(2)	692(6)	52(1)
C(6)	1368(1)	4292(2)	3254(8)	57(1)
C(7)	2709(1)	4514(1)	2396(5)	30(1)
C(8)	2780(1)	4053(1)	3469(5)	32(1)
C(9)	2394(1)	3820(1)	5281(6)	41(1)
C(10)	2475(1)	4202(2)	6661(6)	40(1)
C(11)	2924(1)	4773(1)	6118(5)	34(1)
C(12)	3773(1)	4758(1)	7250(5)	36(1)
C(13)	3653(1)	4085(1)	4888(5)	32(1)
C(14)	4364(1)	4322(1)	7660(5)	31(1)
C(15)	4269(1)	4105(1)	9630(6)	36(1)
C(16)	4688(1)	4064(1)	10624(5)	38(1)
C(17)	5191(1)	4233(1)	9630(6)	38(1)
C(18)	5280(1)	4448(1)	7676(5)	35(1)
C(19)	4868(1)	4502(1)	6662(5)	35(1)

Table S3. Bond lengths [Å] for **13**.

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Br-C (8)	1.945 (3)
N (1)-C (12)	1.384 (4)
N (1)-N (2)	1.447 (3)
N (1)-C (11)	1.487 (4)
N (2)-C (13)	1.398 (4)
N (2)-C (8)	1.475 (4)
N (3)-C (13)	1.389 (4)
N (3)-C (12)	1.396 (4)
N (3)-C (14)	1.438 (4)
O (1)-C (2)	1.340 (5)
O (1)-C (1)	1.458 (5)
O (2)-C (2)	1.189 (5)
O (3)-C (3)	1.419 (3)
O (3)-C (4)	1.446 (4)
O (4)-C (7)	1.408 (4)
O (4)-C (4)	1.432 (4)
O (5)-C (12)	1.193 (4)
O (6)-C (13)	1.210 (4)
C (1)-H (1A)	0.9800
C (1)-H (1B)	0.9800
C (1)-H (1C)	0.9800
C (2)-C (3)	1.523 (5)
C (3)-C (11)	1.538 (5)
C (3)-C (7)	1.557 (4)
C (4)-C (6)	1.491 (5)
C (4)-C (5)	1.524 (5)
C (5)-H (5A)	0.9800
C (5)-H (5B)	0.9800
C (5)-H (5C)	0.9800
C (6)-H (6A)	0.9800
C (6)-H (6B)	0.9800
C (6)-H (6C)	0.9800
C (7)-C (8)	1.555 (4)
C (7)-H (7)	1.0000
C (8)-C (9)	1.501 (5)
C (9)-C (10)	1.320 (5)
C (9)-H (9)	0.9500
C (10)-C (11)	1.490 (5)
C (10)-H (10)	0.9500
C (11)-H (11)	1.0000
C (14)-C (15)	1.378 (5)
C (14)-C (19)	1.390 (4)
C (15)-C (16)	1.385 (5)
C (15)-H (15)	0.9500
C (16)-C (17)	1.390 (5)
C (16)-H (16)	0.9500
C (17)-C (18)	1.368 (5)
C (17)-H (17)	0.9500
C (18)-C (19)	1.391 (4)
C (18)-H (18)	0.9500
C (19)-H (19)	0.9500

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Table S4. Bond angles [deg] for **13**.

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C(12)-N(1)-N(2)	108.9(2)
C(12)-N(1)-C(11)	120.4(3)
N(2)-N(1)-C(11)	113.0(2)
C(13)-N(2)-N(1)	107.1(2)
C(13)-N(2)-C(8)	125.5(2)
N(1)-N(2)-C(8)	109.1(2)
C(13)-N(3)-C(12)	111.9(2)
C(13)-N(3)-C(14)	124.6(2)
C(12)-N(3)-C(14)	123.5(3)
C(2)-O(1)-C(1)	116.4(4)
C(3)-O(3)-C(4)	109.7(2)
C(7)-O(4)-C(4)	110.1(2)
O(1)-C(1)-H(1A)	109.5
O(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
O(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
O(2)-C(2)-O(1)	123.8(3)
O(2)-C(2)-C(3)	124.5(4)
O(1)-C(2)-C(3)	111.7(3)
O(3)-C(3)-C(2)	108.0(2)
O(3)-C(3)-C(11)	109.7(3)
C(2)-C(3)-C(11)	109.6(3)
O(3)-C(3)-C(7)	104.8(2)
C(2)-C(3)-C(7)	116.8(3)
C(11)-C(3)-C(7)	107.7(2)
O(4)-C(4)-O(3)	105.6(2)
O(4)-C(4)-C(6)	109.5(3)
O(3)-C(4)-C(6)	108.0(3)
O(4)-C(4)-C(5)	109.4(3)
O(3)-C(4)-C(5)	110.4(3)
C(6)-C(4)-C(5)	113.6(3)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(4)-C(7)-C(8)	109.5(2)
O(4)-C(7)-C(3)	105.4(2)
C(8)-C(7)-C(3)	108.2(2)
O(4)-C(7)-H(7)	111.2
C(8)-C(7)-H(7)	111.2
C(3)-C(7)-H(7)	111.2
N(2)-C(8)-C(9)	110.6(3)
N(2)-C(8)-C(7)	104.2(2)
C(9)-C(8)-C(7)	110.3(2)
N(2)-C(8)-Br	110.71(19)
C(9)-C(8)-Br	113.0(2)
C(7)-C(8)-Br	107.7(2)
C(10)-C(9)-C(8)	112.5(3)
C(10)-C(9)-H(9)	123.8
C(8)-C(9)-H(9)	123.8
C(9)-C(10)-C(11)	114.4(3)
C(9)-C(10)-H(10)	122.8
C(11)-C(10)-H(10)	122.8
N(1)-C(11)-C(10)	109.4(2)

N(1)-C(11)-C(3)	101.9(3)
C(10)-C(11)-C(3)	111.3(3)
N(1)-C(11)-H(11)	111.3
C(10)-C(11)-H(11)	111.3
C(3)-C(11)-H(11)	111.3
O(5)-C(12)-N(1)	126.2(3)
O(5)-C(12)-N(3)	128.6(3)
N(1)-C(12)-N(3)	105.2(3)
O(6)-C(13)-N(3)	126.1(3)
O(6)-C(13)-N(2)	128.0(3)
N(3)-C(13)-N(2)	105.8(2)
C(15)-C(14)-C(19)	121.7(3)
C(15)-C(14)-N(3)	119.6(3)
C(19)-C(14)-N(3)	118.6(3)
C(14)-C(15)-C(16)	118.7(3)
C(14)-C(15)-H(15)	120.6
C(16)-C(15)-H(15)	120.6
C(15)-C(16)-C(17)	120.2(3)
C(15)-C(16)-H(16)	119.9
C(17)-C(16)-H(16)	119.9
C(18)-C(17)-C(16)	120.6(3)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(17)-C(18)-C(19)	120.2(3)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
C(14)-C(19)-C(18)	118.6(3)
C(14)-C(19)-H(19)	120.7
C(18)-C(19)-H(19)	120.7

---

Table S5. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **13**.  
The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Br	49(1)	43(1)	40(1)	-13(1)	-11(1)	25(1)
N(1)	34(1)	40(1)	29(1)	-8(1)	-8(1)	25(1)
N(2)	32(1)	37(1)	29(1)	-6(1)	-7(1)	22(1)
N(3)	35(1)	43(1)	28(1)	-7(1)	-6(1)	26(1)
O(1)	53(1)	39(1)	56(2)	7(1)	10(1)	18(1)
O(2)	63(2)	44(1)	61(2)	-12(1)	-15(2)	22(1)
O(3)	33(1)	51(1)	41(1)	-9(1)	-8(1)	28(1)
O(4)	38(1)	49(1)	45(2)	-9(1)	-14(1)	27(1)
O(5)	54(1)	65(2)	41(2)	-22(1)	-22(1)	42(1)
O(6)	48(1)	44(1)	37(1)	-5(1)	-4(1)	31(1)
C(1)	74(3)	45(2)	96(4)	21(2)	30(3)	15(2)
C(2)	39(2)	40(2)	50(2)	-5(2)	-4(2)	25(2)
C(3)	34(2)	43(2)	33(2)	-3(1)	-2(1)	25(1)
C(4)	38(2)	49(2)	36(2)	-5(2)	-10(1)	26(2)
C(5)	56(2)	59(2)	50(2)	3(2)	-10(2)	36(2)
C(6)	38(2)	69(2)	66(3)	-7(2)	-4(2)	28(2)
C(7)	29(1)	40(2)	25(2)	0(1)	-4(1)	21(1)
C(8)	33(1)	34(2)	30(2)	2(1)	-1(1)	18(1)
C(9)	36(2)	43(2)	41(2)	4(2)	-1(2)	19(2)
C(10)	41(2)	60(2)	26(2)	-3(2)	-2(1)	31(2)
C(11)	37(2)	47(2)	29(2)	-3(1)	-3(1)	28(1)
C(12)	37(2)	44(2)	33(2)	-8(1)	-11(1)	25(1)
C(13)	35(1)	39(2)	26(2)	0(1)	3(1)	22(1)
C(14)	29(1)	39(2)	31(2)	-2(1)	-4(1)	22(1)
C(15)	35(2)	40(2)	37(2)	7(2)	6(2)	22(1)
C(16)	41(2)	43(2)	31(2)	9(1)	4(1)	23(1)
C(17)	37(2)	44(2)	39(2)	8(2)	-4(2)	24(1)
C(18)	33(2)	41(2)	35(2)	7(1)	5(1)	22(1)
C(19)	40(2)	44(2)	27(2)	2(1)	-1(1)	26(1)

Table S6. Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **13**.

	x	y	z	U(eq)
H(1A)	3660	6471	1488	117
H(1B)	3780	6233	-580	117
H(1C)	4129	6299	1469	117
H(5A)	2376	5267	312	77
H(5B)	1829	5258	1144	77
H(5C)	1778	4806	-507	77
H(6A)	1372	4061	4391	86
H(6B)	1127	4054	2145	86
H(6C)	1228	4532	3757	86
H(7)	2970	4680	1204	36
H(9)	2121	3438	5419	49
H(10)	2264	4121	7898	48
H(11)	2983	5043	7245	41
H(15)	3923	3986	10293	43
H(16)	4631	3919	11988	45
H(17)	5474	4198	10313	46
H(18)	5625	4562	7009	42
H(19)	4930	4658	5316	41

Table S7. Crystal data and structure refinement for **21**.

Identification code	h10sel3
Empirical formula	C14 H13 Br Fe O7
Formula weight	429.00
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P 2_1 2_1 2_1$
Unit cell dimensions	a = 8.6252(3) Å    alpha = 90 deg. b = 8.6773(3) Å    beta = 90 deg. c = 43.7286(16) Å    gamma = 90 deg.
Volume	3272.8(2) Å <sup>3</sup>
Z, Calculated density	8, 1.741 Mg/m <sup>3</sup>
Absorption coefficient	3.394 mm <sup>-1</sup>
F(000)	1712
Crystal size	0.45 x 0.30 x 0.15 mm
Theta range for data collection	3.31 to 27.56 deg.
Limiting indices	-11 ≤ h ≤ 11, -10 ≤ k ≤ 11, -56 ≤ l ≤ 56
Reflections collected / unique	25844 / 6937 [R(int) = 0.0663]
Completeness to theta = 27.56	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6300 and 0.3104
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	6937 / 0 / 429
Goodness-of-fit on F <sup>2</sup>	1.063
Final R indices [I > 2σ(I)]	R1 = 0.0437, wR2 = 0.0788
R indices (all data)	R1 = 0.0677, wR2 = 0.0860
Absolute structure parameter	0.011(9)
Largest diff. peak and hole	0.554 and -0.567 e.Å <sup>-3</sup>

Table S8. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **21**.  
 $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U(\text{eq})$
Fe(1)	10630(1)	3004(1)	1789(1)	29(1)
C(10)	11952(6)	4506(7)	1691(1)	37(1)
O(10)	12725(4)	5543(5)	1637(1)	55(1)
C(20)	9414(5)	3129(5)	1460(1)	33(1)
O(20)	8621(4)	3203(5)	1252(1)	48(1)
C(30)	11935(7)	1555(7)	1656(1)	49(1)
O(30)	12798(6)	659(6)	1564(1)	82(2)
Br(1)	9092(1)	-631(1)	1945(1)	40(1)
O(1)	5849(4)	4037(4)	1661(1)	45(1)
O(2)	7164(4)	6167(4)	1767(1)	34(1)
O(3)	6991(3)	4460(4)	2354(1)	26(1)
O(4)	7042(3)	1862(4)	2372(1)	32(1)
C(1)	7613(5)	2229(5)	2075(1)	25(1)
C(2)	9181(5)	1552(5)	2031(1)	28(1)
C(3)	10416(5)	2056(5)	2218(1)	27(1)
C(4)	10515(5)	3662(5)	2237(1)	27(1)
C(5)	9388(5)	4487(6)	2071(1)	26(1)
C(6)	7726(5)	4003(5)	2075(1)	24(1)
C(7)	6801(5)	4696(5)	1809(1)	27(1)
C(8)	6394(5)	6928(6)	1514(1)	39(1)
C(9)	6190(5)	3148(5)	2481(1)	29(1)
C(11)	6334(6)	3219(7)	2823(1)	43(1)
C(12)	4525(5)	3111(6)	2376(1)	40(1)
Fe(2)	10537(1)	8236(1)	709(1)	31(1)
C(40)	12113(8)	9453(7)	814(1)	49(1)
C(50)	10325(5)	7159(6)	1058(1)	34(1)
C(60)	9096(8)	9641(7)	804(1)	52(2)
O(40)	13210(6)	10130(5)	881(1)	80(2)
O(50)	10073(5)	6542(4)	1279(1)	54(1)
O(60)	8167(6)	10514(6)	869(1)	86(2)
Br(2)	6891(1)	6719(1)	544(1)	39(1)
O(5)	11603(4)	3692(5)	904(1)	59(1)
O(6)	13814(4)	4496(4)	706(1)	36(1)
O(7)	11983(3)	4543(4)	163(1)	27(1)
O(8)	9357(4)	4498(4)	165(1)	34(1)
C(21)	9769(5)	5174(5)	451(1)	27(1)
C(22)	9099(5)	6770(5)	470(1)	29(1)
C(23)	9665(5)	7941(5)	278(1)	29(1)
C(24)	11290(6)	8018(5)	265(1)	32(1)
C(25)	12078(6)	6912(6)	448(1)	29(1)
C(26)	11539(5)	5273(5)	446(1)	24(1)
C(27)	12292(5)	4390(5)	715(1)	25(1)
C(28)	14656(6)	3757(6)	952(1)	37(1)
C(29)	10673(5)	3691(5)	53(1)	29(1)
C(31)	10679(7)	3765(6)	-290(1)	47(1)
C(32)	10713(6)	2062(5)	174(1)	44(1)



Table S9. Bond lengths [Å] for **21**.

---

Fe(1)-C(30)	1.785(6)
Fe(1)-C(10)	1.785(6)
Fe(1)-C(20)	1.785(5)
Fe(1)-C(4)	2.044(4)
Fe(1)-C(3)	2.054(4)
Fe(1)-C(2)	2.066(5)
Fe(1)-C(5)	2.079(5)
C(10)-O(10)	1.143(6)
C(20)-O(20)	1.141(5)
C(30)-O(30)	1.149(6)
Br(1)-C(2)	1.933(4)
O(1)-C(7)	1.193(5)
O(2)-C(7)	1.326(5)
O(2)-C(8)	1.451(5)
O(3)-C(6)	1.432(5)
O(3)-C(9)	1.444(5)
O(4)-C(9)	1.420(5)
O(4)-C(1)	1.423(5)
C(1)-C(2)	1.487(6)
C(1)-C(6)	1.543(6)
C(2)-C(3)	1.410(6)
C(3)-C(4)	1.399(6)
C(4)-C(5)	1.410(6)
C(5)-C(6)	1.494(6)
C(5)-H(5)	0.85(4)
C(6)-C(7)	1.532(6)
C(9)-C(11)	1.500(6)
C(9)-C(12)	1.509(6)
Fe(2)-C(40)	1.782(7)
Fe(2)-C(60)	1.790(6)
Fe(2)-C(50)	1.799(5)
Fe(2)-C(23)	2.042(4)
Fe(2)-C(24)	2.057(5)
Fe(2)-C(22)	2.061(4)
Fe(2)-C(25)	2.096(5)
C(40)-O(40)	1.151(7)
C(50)-O(50)	1.125(5)
C(60)-O(60)	1.139(7)
Br(2)-C(22)	1.933(4)
O(5)-C(27)	1.184(5)
O(6)-C(27)	1.317(5)
O(6)-C(28)	1.447(5)
O(7)-C(29)	1.433(5)
O(7)-C(26)	1.441(5)
O(8)-C(29)	1.421(5)
O(8)-C(21)	1.426(5)
C(21)-C(22)	1.503(6)
C(21)-C(26)	1.528(6)
C(22)-C(23)	1.404(6)
C(23)-C(24)	1.405(7)
C(24)-C(25)	1.422(7)
C(25)-C(26)	1.496(7)
C(25)-H(25)	0.93(4)
C(26)-C(27)	1.547(6)
C(29)-C(31)	1.500(6)
C(29)-C(32)	1.509(6)

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Table S10. Bond lengths [Å] and angles [deg] for **21**.

---

C (30)-Fe (1)-C (10)	91.9 (2)
C (30)-Fe (1)-C (20)	98.7 (2)
C (10)-Fe (1)-C (20)	97.8 (2)
C (30)-Fe (1)-C (4)	122.7 (2)
C (10)-Fe (1)-C (4)	93.3 (2)
C (20)-Fe (1)-C (4)	136.7 (2)
C (30)-Fe (1)-C (3)	94.1 (2)
C (10)-Fe (1)-C (3)	124.7 (2)
C (20)-Fe (1)-C (3)	135.03 (19)
C (4)-Fe (1)-C (3)	39.93 (17)
C (30)-Fe (1)-C (2)	96.8 (2)
C (10)-Fe (1)-C (2)	162.8 (2)
C (20)-Fe (1)-C (2)	95.5 (2)
C (4)-Fe (1)-C (2)	69.49 (17)
C (3)-Fe (1)-C (2)	40.01 (17)
C (30)-Fe (1)-C (5)	162.6 (2)
C (10)-Fe (1)-C (5)	91.1 (2)
C (20)-Fe (1)-C (5)	97.92 (19)
C (4)-Fe (1)-C (5)	39.97 (17)
C (3)-Fe (1)-C (5)	70.20 (18)
C (2)-Fe (1)-C (5)	76.24 (18)
O (10)-C (10)-Fe (1)	175.0 (5)
O (20)-C (20)-Fe (1)	179.1 (4)
O (30)-C (30)-Fe (1)	177.6 (5)
C (7)-O (2)-C (8)	115.8 (4)
C (6)-O (3)-C (9)	108.9 (3)
C (9)-O (4)-C (1)	108.1 (3)
O (4)-C (1)-C (2)	110.1 (3)
O (4)-C (1)-C (6)	104.3 (4)
C (2)-C (1)-C (6)	109.7 (4)
C (3)-C (2)-C (1)	119.4 (4)
C (3)-C (2)-Br (1)	116.6 (3)
C (1)-C (2)-Br (1)	112.1 (3)
C (3)-C (2)-Fe (1)	69.5 (3)
C (1)-C (2)-Fe (1)	112.0 (3)
Br (1)-C (2)-Fe (1)	121.4 (2)
C (4)-C (3)-C (2)	113.0 (4)
C (4)-C (3)-Fe (1)	69.6 (3)
C (2)-C (3)-Fe (1)	70.4 (3)
C (3)-C (4)-C (5)	115.6 (4)
C (3)-C (4)-Fe (1)	70.4 (3)
C (5)-C (4)-Fe (1)	71.4 (3)
C (4)-C (5)-C (6)	120.9 (4)
C (4)-C (5)-Fe (1)	68.7 (3)
C (6)-C (5)-Fe (1)	109.1 (3)
O (3)-C (6)-C (5)	110.9 (3)
O (3)-C (6)-C (7)	107.9 (3)
C (5)-C (6)-C (7)	112.4 (4)
O (3)-C (6)-C (1)	104.3 (4)
C (5)-C (6)-C (1)	109.9 (4)
C (7)-C (6)-C (1)	111.1 (4)
O (1)-C (7)-O (2)	123.3 (4)
O (1)-C (7)-C (6)	125.6 (4)
O (2)-C (7)-C (6)	111.1 (4)
O (4)-C (9)-O (3)	104.0 (3)
O (4)-C (9)-C (11)	109.0 (4)
O (3)-C (9)-C (11)	108.3 (4)
O (4)-C (9)-C (12)	111.9 (4)
O (3)-C (9)-C (12)	110.7 (4)
C (11)-C (9)-C (12)	112.6 (4)
C (40)-Fe (2)-C (60)	93.8 (3)
C (40)-Fe (2)-C (50)	99.6 (2)
C (60)-Fe (2)-C (50)	95.0 (2)
C (40)-Fe (2)-C (23)	126.4 (2)
C (60)-Fe (2)-C (23)	92.5 (2)

C (50) -Fe (2) -C (23)	132.8 (2)
C (40) -Fe (2) -C (24)	93.3 (2)
C (60) -Fe (2) -C (24)	120.1 (2)
C (50) -Fe (2) -C (24)	141.8 (2)
C (23) -Fe (2) -C (24)	40.08 (18)
C (40) -Fe (2) -C (22)	162.9 (2)
C (60) -Fe (2) -C (22)	96.9 (2)
C (50) -Fe (2) -C (22)	92.8 (2)
C (23) -Fe (2) -C (22)	40.00 (18)
C (24) -Fe (2) -C (22)	69.78 (18)
C (40) -Fe (2) -C (25)	88.9 (2)
C (60) -Fe (2) -C (25)	160.1 (2)
C (50) -Fe (2) -C (25)	104.0 (2)
C (23) -Fe (2) -C (25)	70.30 (18)
C (24) -Fe (2) -C (25)	40.04 (18)
C (22) -Fe (2) -C (25)	76.53 (17)
O (40) -C (40) -Fe (2)	174.2 (6)
O (50) -C (50) -Fe (2)	174.2 (4)
O (60) -C (60) -Fe (2)	178.4 (6)
C (27) -O (6) -C (28)	116.6 (4)
C (29) -O (7) -C (26)	107.8 (3)
C (29) -O (8) -C (21)	107.8 (3)
O (8) -C (21) -C (22)	109.3 (4)
O (8) -C (21) -C (26)	105.1 (4)
C (22) -C (21) -C (26)	109.5 (4)
C (23) -C (22) -C (21)	120.1 (4)
C (23) -C (22) -Br (2)	117.4 (3)
C (21) -C (22) -Br (2)	111.5 (3)
C (23) -C (22) -Fe (2)	69.3 (3)
C (21) -C (22) -Fe (2)	111.4 (3)
Br (2) -C (22) -Fe (2)	121.4 (2)
C (22) -C (23) -C (24)	114.0 (4)
C (22) -C (23) -Fe (2)	70.7 (3)
C (24) -C (23) -Fe (2)	70.5 (3)
C (23) -C (24) -C (25)	114.9 (4)
C (23) -C (24) -Fe (2)	69.4 (3)
C (25) -C (24) -Fe (2)	71.5 (3)
C (24) -C (25) -C (26)	119.3 (4)
C (24) -C (25) -Fe (2)	68.5 (3)
C (26) -C (25) -Fe (2)	109.0 (3)
O (7) -C (26) -C (25)	109.8 (3)
O (7) -C (26) -C (21)	104.7 (4)
C (25) -C (26) -C (21)	111.4 (4)
O (7) -C (26) -C (27)	108.9 (3)
C (25) -C (26) -C (27)	109.6 (4)
C (21) -C (26) -C (27)	112.3 (4)
O (5) -C (27) -O (6)	123.8 (4)
O (5) -C (27) -C (26)	125.0 (4)
O (6) -C (27) -C (26)	111.2 (4)
O (8) -C (29) -O (7)	105.1 (3)
O (8) -C (29) -C (31)	109.0 (4)
O (7) -C (29) -C (31)	108.1 (4)
O (8) -C (29) -C (32)	111.0 (4)
O (7) -C (29) -C (32)	110.4 (4)
C (31) -C (29) -C (32)	112.9 (4)

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Table S11. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **21**.  
The anisotropic displacement factor exponent takes the form:  
 $-2 \pi^2 [ h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12} ]$

	U11	U22	U33	U23	U13	U12
Fe(1)	30(1)	36(1)	20(1)	-1(1)	1(1)	3(1)
C(10)	29(3)	52(3)	32(3)	-6(3)	-4(2)	2(3)
O(10)	37(2)	68(3)	59(3)	3(2)	3(2)	-20(2)
C(20)	37(3)	30(3)	32(3)	-5(2)	11(2)	-6(3)
O(20)	48(2)	76(3)	19(2)	0(2)	-8(2)	-13(2)
C(30)	58(3)	61(4)	27(3)	6(3)	15(3)	19(3)
O(30)	109(4)	78(3)	58(3)	13(3)	42(3)	52(3)
Br(1)	59(1)	28(1)	34(1)	-3(1)	-5(1)	7(1)
O(1)	46(2)	37(2)	53(2)	3(2)	-30(2)	-7(2)
O(2)	37(2)	30(2)	33(2)	9(1)	-10(2)	-9(2)
O(3)	24(2)	28(2)	25(2)	0(1)	3(1)	-1(2)
O(4)	31(2)	28(2)	35(2)	6(2)	7(2)	2(2)
C(1)	24(2)	26(3)	23(2)	2(2)	-2(2)	-2(2)
C(2)	40(3)	26(2)	18(2)	-1(2)	-2(2)	0(2)
C(3)	30(2)	37(3)	15(2)	2(2)	3(2)	7(2)
C(4)	26(2)	38(3)	18(2)	-5(2)	-3(2)	-2(2)
C(5)	24(2)	29(3)	24(2)	-4(2)	1(2)	-8(2)
C(6)	22(2)	31(3)	19(2)	1(2)	-3(2)	1(2)
C(7)	28(2)	29(3)	24(2)	0(2)	-1(2)	-1(2)
C(8)	42(3)	34(3)	40(3)	13(2)	-11(2)	-6(2)
C(9)	26(2)	28(3)	33(2)	1(2)	5(2)	-1(2)
C(11)	39(3)	56(3)	34(3)	6(3)	9(2)	2(3)
C(12)	28(3)	40(3)	53(3)	4(3)	2(2)	-6(3)
Fe(2)	48(1)	24(1)	21(1)	0(1)	-1(1)	1(1)
C(40)	82(4)	32(3)	32(3)	2(3)	8(3)	-9(4)
C(50)	40(3)	35(3)	27(3)	1(2)	1(2)	3(2)
C(60)	79(4)	46(4)	33(3)	-8(3)	-19(3)	11(4)
O(40)	101(4)	79(4)	58(3)	-20(2)	6(3)	-54(3)
O(50)	72(3)	53(3)	36(2)	16(2)	7(2)	-2(2)
O(60)	108(4)	73(3)	76(4)	-33(3)	-25(3)	54(3)
Br(2)	34(1)	50(1)	33(1)	4(1)	2(1)	11(1)
O(5)	34(2)	84(3)	59(3)	46(2)	7(2)	4(2)
O(6)	34(2)	39(2)	33(2)	9(2)	-10(2)	-1(2)
O(7)	29(2)	30(2)	22(2)	-1(1)	3(1)	-3(2)
O(8)	33(2)	29(2)	39(2)	-10(2)	-7(2)	0(2)
C(21)	33(3)	20(2)	29(3)	1(2)	2(2)	2(2)
C(22)	32(2)	32(2)	22(2)	-2(2)	-1(2)	3(2)
C(23)	37(3)	30(3)	21(2)	-1(2)	-1(2)	9(2)
C(24)	52(3)	20(2)	23(2)	2(2)	5(2)	-4(2)
C(25)	28(2)	25(3)	32(2)	2(2)	3(2)	-3(2)
C(26)	27(3)	23(3)	23(2)	0(2)	3(2)	0(2)
C(27)	28(3)	26(2)	22(2)	1(2)	-2(2)	2(2)
C(28)	39(3)	37(3)	34(3)	2(2)	-19(2)	0(2)
C(29)	30(2)	26(2)	30(3)	-3(2)	-2(2)	-2(2)
C(31)	57(3)	51(3)	34(3)	-6(2)	-11(3)	-11(3)
C(32)	44(3)	21(2)	67(4)	-3(2)	5(3)	0(2)

Table S12. Hydrogen coordinates (  $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **21**.

	x	y	z	U (eq)
H (1)	6883	1862	1913	30
H (3)	11108	1375	2319	33
H (4)	11291	4164	2355	33
H (8A)	6639	6388	1323	58
H (8B)	6753	7998	1500	58
H (8C)	5271	6914	1547	58
H (11A)	5835	2313	2913	65
H (11B)	5829	4155	2899	65
H (11C)	7433	3234	2880	65
H (12A)	4493	2989	2153	61
H (12B)	4012	4078	2433	61
H (12C)	3988	2244	2473	61
H (21)	9404	4523	625	33
H (23)	9008	8622	168	35
H (24)	11823	8752	142	38
H (28A)	14395	4257	1147	55
H (28B)	15772	3849	915	55
H (28C)	14370	2665	962	55
H (31A)	9735	3281	-369	71
H (31B)	11589	3218	-369	71
H (31C)	10717	4844	-355	71
H (32A)	10663	2080	397	66
H (32B)	11676	1561	109	66
H (32C)	9824	1487	93	66
H (25)	13140 (50)	7050 (50)	436 (9)	17 (10)
H (5)	9480 (40)	5460 (50)	2082 (9)	13 (11)